

April, 1936

RUBBER CHEMISTRY AND TECHNOLOGY

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VOLUME IX

NUMBER 2

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RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the editor representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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New Books and Other Publications

The Chemistry of Rubber. By H. Freundlich, University College, London. Methuen and Company, Ltd., 36 Essex Street, W. C., London, England, 1935. xi + 72 pp. 13 figs. 11×17.5 cm. Price, 2s./6d., net.

The author, internationally known as one of the outstanding scientists of the day in colloid chemistry, offers in the present booklet a highly condensed, but nevertheless precise and clearly written treatise on the chemistry of rubber. The book is divided into three main chapters.

In the first one, "Latex," the most striking colloid chemical reactions as, for example, particle structure, electrophoresis, concentration, coagulation, and briefly industrial application, are discussed; this is followed by an excellent summary of the results and interpretations of x-ray research, mastication, swelling and solubility, vulcanization, and oxidation of crude rubber. The influence of fillers when incorporated into rubber receives an especially noteworthy discussion.

Not only does Freundlich give us the latest information in regard to our knowledge of rubber chemistry, conclusively pointing out the importance of colloid chemistry, but he also draws attention to a few unsolved problems and how they might be successfully tackled.

The last chapter discusses from a colloidal point of view the botany of the latex origin, and gives a brief survey on the historical development of the rubber industry.

To all who want to obtain a concentrated picture as to where we stand now in our knowledge of rubber chemistry, the book should prove of great value.

(On page 15 the statement that rubberized cord makes up the cover of a tire should be corrected. It is the carcass where it is used which gives the tire the rigidity needed onto which the cover or tread is applied. On page 16 the statement that latex threads show a greater resistance toward chafing seems somewhat too positive. Cut thread if properly cured will chafe less, as should be expected by the more uniform structure of milled rubber. On page 48 low temperature cures using accelerators seem to have been confused with the so-called "cold" or "vapor" cures using S_2Cl_2 in solution or in vapor form as vulcanizing agent.) [E. A. Hauser in the *Journal of the American Chemical Society*.]

Rubber. Some Facts on Its History, Production, and Manufacture. Prepared by P. W. Barker. Department of Commerce, Bureau of Foreign and Domestic Commerce, Leather and Rubber Division, Washington, D. C. January, 1936. Paper, 26 pages, 8 by $10\frac{1}{4}$ inches. Illustrated.

This publication has been prepared in response to numerous requests from students and the public for information on the production of rubber and the manufacture of rubber products. The origin and progress of the industry is presented on the following well conceived plan: I. Definition; II. History; III. Production—A. Plantation Rubber, B. Wild Rubber, C. Government Control; IV. Consumption—A. Manufacture, B. United States Industry, C. Foreign Industry, D. Reclaimed Rubber, E. Synthetic Rubber; V. Illustrations; VI. Statistics. [From the *India Rubber World*.]

Sur La Saignée de L'Hevea. By Francois-J. Gain. Published by Imprimerie Georges Thomas, Solignac and Henri-Lepage Streets, Nancy, France. 162 pp. 30 francs.

Written in French, this book is devoted to methods of tapping rubber trees. It consists of an introduction, three chapters, and a section devoted to the author's general conclusions on the tapping methods discussed. The history of tapping,

from early crude methods to the technically controlled methods now in use, is covered. The subject matter is of particular interest to rubber cultivators, of course, but should also prove of interest to rubber manufacturers. [From *The Rubber Age* of N. Y.]

A Rubber Plantation in New Jersey. Prepared and published by the Thiokol Corporation, Yardville, N. J.

The story of synthetic rubber is excellently told by this little booklet, written in interesting style. The events leading up to the commercialization of Thiokol, starting with the mixing of dichloroethane and sodium polysulfide by J. C. Patrick, now chief chemist of the Thiokol Corporation, are briefly outlined. Major differences in the chemical characteristics and properties of synthetic and crude rubber are discussed. The many uses to which synthetic rubbers have already been put, such as tubing, cables, fuel hose, printing plates, etc., are described, with intimations of further uses. A series of clever black and white illustrations add to the attractiveness of the text. This booklet is recommended to all those in the rubber industry still unfamiliar with the background and potential applications of synthetic rubber—Thiokol in particular. [From *The Rubber Age* of N. Y.]

Latex in Industry. By Royce J. Noble. Published by The Rubber Age. 250 West 57th Street, New York City. 384 pp. \$7.00 per copy.

The book is divided into two parts. Part I consists of ten chapters, covering the sources, preservation, shipment, properties and concentration of latex, artificial latices, vulcanized latices, the compounding, coagulation, vulcanization and examination of latex, and the evolution of specifications for the consumer.

Part II consists of fourteen chapters, dealing with individual processes of present-day industrial application. It is quite the best handling of this subject which we have seen. In his preface the author states that his effort has been to give the beginner a foundation in latex technology, and at the same time to furnish the more experienced worker with detailed information which will be helpful in developing present processes, or in research on new applications. To attain these two objectives in one volume is no easy task, but Dr. Noble has succeeded. Thus, for example, his treatment of the properties of colloids in general is simpler than usual, while his chapters on compounding include material of an advanced character. The elementary and the advanced work develop smoothly.

The book is well illustrated, though some of the illustrations appear redundant, and others fail in their instructiveness through being insufficiently described.

There are inaccuracies, *e. g.*, on page 19 "the incision is made as deep as possible into the inner bark and to within 1 mm. of the cambium; the bark is used more sparingly than a few inches a month;" there are also omissions, *e. g.*, the rather fragmentary references to the theory of the two steps in the coagulation process, to dialysis, etc., but these are small matters. On the other hand, we wonder whether the author has appreciated how much more valuable his book might have been to the student if it had been text-referenced. While appreciating the difficulties which beset an author in carrying the reader through a maze of patent references, the fact that much of the technology of latex first appears as patent literature, *e. g.*, practically the whole of his chapter on artificial latices, the value of a text-referenced account is obvious.

The author has succeeded in accomplishing well what he set out to do, but a reading of his book makes one wonder all the more whether the time has arrived when anyone but an expert can handle the product to its maximum advantage, and whether for the time being at any rate technical advice in using the material is not the limiting factor of industrial consumption.

The book should be eagerly sought by all engaged in latex technology. [From the *Bulletin of the Rubber Growers' Association.*]

Chlorinated Hydrocarbons. Issued by the R. & H. Chemicals Dept., E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware.

This technical bulletin lists the characteristics, properties, specifications, and other useful information on chlorinated hydrocarbons, sixteen of which are included, all of them being in commercial use. These products are non-flammable and non-explosive, with the exception of a few which are moderately flammable. Some of these chlorinated hydrocarbons are liquid, others are gaseous at ordinary temperatures, while one is a solid. The bulletin provides information on flammability, classification, stability, effect on common engineering metals, selective solvent action, and commercial properties. Other data necessary to the selection and use of these products for specific purposes are also given. [From *The Rubber Age* of N. Y.]

Some Aspects of Propaganda in the Rubber Industry. By James Fairbairn. (A reprint.) Issued by the Rubber Growers' Association, Inc., 19, Fenchurch Street, London, E. C. 3, England.

A reprint of an address given by Mr. Fairbairn on November 25, 1935, before the London Section of the I. R. I., this paper discusses the various methods open to use by members of the rubber industry to publicize their products and thus create wider markets. He discusses several methods, including advertising, distribution of literature, participation in exhibitions, conferences and lectures, and experimental work connected with possible new uses. Methods followed by the Rubber Growers' Association are outlined briefly. [From *The Rubber Age* of N. Y.]

Asiatic Production. Supplement to "The Truth About Restriction." By L. W. Holland. Published by Kelly & Walsh, Ltd., Raffles Place, Singapore, F. M. S.

Added to the author's book "The Truth About Restriction" after it had been published, this supplement treats with native, or Asiatic, production. It continues the author's demands for the inauguration of a six-day week on rubber plantations, including those devoted to native or "Asiatic" production. Mr. Holland takes the stand that European producers are responsible for the seven-day week, and therefore should "adopt the six-day week and reduce their own production first." As in the original booklet, the author repeats his theory that restriction is based "on figures only and not on any sound principle." Adoption of the six-day week will in his opinion remove the "inequalities of restriction." [From *The Rubber Age* of N. Y.]

Ace Hard Rubber Protection (For Chemical Process Industries). Distributed by the American Hard Rubber Company, 11 Mercer Street, New York City. 64 pp.

The complete line of rubber linings featured by American Hard Rubber, including those for steel tanks, tank cars, pipes, pumps, utensils, and other products, is described in this attractively put-together catalog. A list of solutions to which these linings offer corrosion resistance is given. Instructions for applying the linings in several instances are outlined. Dimensions are given of many Ace Hard Rubber pumps. Several utensils for acid handling, such as pails, dippers, beakers, bottles, etc., are described and illustrated. One section briefly describes the Anode Process. Weights of hard rubber rods, sheets, and tubes are printed, as are the physical, chemical, and electrical properties of hard rubber. The catalog is replete with information on hard rubber and its uses. [From *The Rubber Age* of N. Y.]

A.S.T.M. Standards on Textile Materials. Prepared by Committee D-13. Published by the American Society for Testing Materials, 260 S. Broad Street, Philadelphia, Penna. 246 pp. \$1.50.

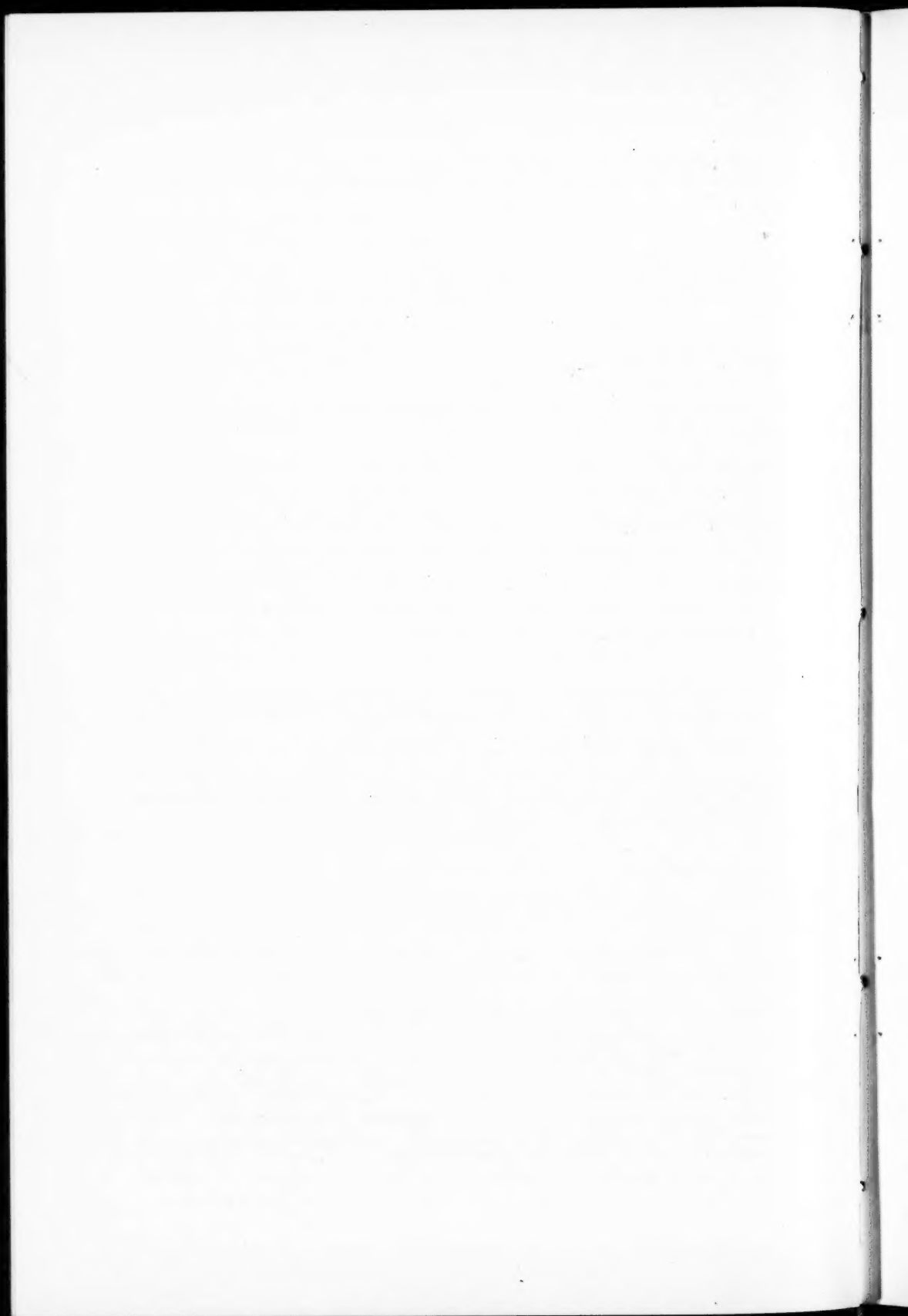
All of the 37 standard specifications and tests which have been developed by Committee D-13 are contained in this compilation of A.S.T.M. standards on textile materials. In addition to these standards and tests, there are given a proposed potassium dichromate oxidation method for the determination of total iron in asbestos textiles, several proposed methods of tests for fastness and slippage, a yarn number conversion table, and a psychrometric table for relative humidity. A large number of textile products are covered in the compilation, including electrical tape. Abstracts of papers presented at D-13 meetings during the past year are also included. [From *The Rubber Age* of N. Y.]

Index to A.S.T.M. Standards and Tentative Standards, January 1, 1936. American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa.

The index is of service in ascertaining whether the Society has issued any standard specifications or test methods covering particular engineering materials or subjects, and also in finding conveniently any of the standards in the publications where they appear. The latest edition gives information on all of the 794 A.S.T.M. standards and tentative standards as of January 1, 1936. All items are listed in the index under appropriate key-words, according to the particular subjects they cover. As a convenience, a list is given of the specifications and tests in numeric sequence of their serial designations. Copies of this publication are furnished without charge on written request. [From the *India Rubber World*.]

Apparatus for Testing Petroleum Products. (Catalog No. 160.) Prepared and distributed by the Precision Scientific Company, 1749 North Springfield Avenue, Chicago.

In addition to containing specifications and references to governing standards, notably those of the A.S.T.M., this catalog is compiled and arranged for quick, convenient reference on all types of apparatus involved in testing petroleum products. An A.S.T.M. reference index is included, which indicates the apparatus necessary for each designation. Information on general utility equipment for the laboratory, such as burners, heaters and hot plates, constant temperature baths, etc., is also part of this catalog. [From *The Rubber Age* of N. Y.]



Uniform Vulcanization

Henri Leduc

All rubber technologists are familiar from experience with the difficulties of vulcanizing objects which are bulky, thick, or porous, and they are as well informed as the writer on this problem.

The properties of a vulcanizate reach their maximum at a certain cure which is defined by a certain temperature and a certain time. Rubber is a very poor conductor of heat, and up to the present time it has been necessary in order to cure it to have the surface of the object in contact with a hot fluid or a hot surface, in which case the heat penetrates with difficulty into the mass, and its distribution is far from uniform.

It is clear therefore that the uniform curing of large masses is almost impossible in spite of any artifice employed. To make evident the order of magnitude of the differences in the state of cure, two experiments will be described.

(1) A cylindrical iron mold, 105 millimeters in diameter and 60 millimeters high, was constructed with a cavity for a thermometer at its middle point. The mold was filled with a mixture composed of:

Rubber	100
Stearic acid	1
Zinc oxide	10
Sulfur	3
Accelerator "808"	1

The filled mold was placed between the platens of a press heated to 135° C. At this temperature the correct vulcanization of a thin sheet of this mixture would require about 20-25 minutes.

The curve of the temperature as a function of the time (Fig. 1) shows that the center of the sample increased at an average of 1° C. per minute. Thus, in order for the center of the sample to increase above the surrounding temperature of 20° C. to a temperature of 120° a little over 100 minutes was required. At approximately three centimeters from the hot platens the temperature did not change until after ten minutes, and after 60 minutes of heating the lag was such that the center of the sample was still far from being constant, while the surface had twice its cure. If a satisfactory cure of the center is desired, it must be kept in the press a length of time equal to four times the normal time of cure for this mixture.

It should be noted that an accelerator that was not too active was chosen purposely, for with a mixture with a high rate of vulcanization, i. e., 10 to 20 minutes, the difference between the vulcanization at the center and that at the surface would have been much greater.

It is therefore necessary to choose between a suitably vulcanized surface with an almost raw center, or a terribly overvulcanized surface with a correct center. As a matter of fact, this incongruous state of affairs has to be tolerated, and efforts are made to improve conditions by the use of slow accelerators with a long plateau, by step increases in the temperature and by other means.

Whatever the method may be, the results are often unsatisfactory and always troublesome, for the output of vulcanized product is extremely low and the mechani-

cal properties of mixtures with slow rates of vulcanization are always inferior to those of mixtures which vulcanize rapidly.

(2) In a second experiment an iron mold 10 centimeters in diameter and only 4 centimeters high was used. A sheet of a sponge mixture was placed in the mold, which was then heated in a press to 140°C . The temperature at the center of the sample, *i. e.*, two centimeters from the heating plate, showed after 30 minutes a lag of 25° with respect to the surface. In the beginning the heating was more rapid than in the preceding experiment, because of the smaller distance between the platens and because the mass to be heated was less in proportion to the heating surface, but as soon as the cellular structure was formed the condition of the mass obviously greatly magnified the poor distribution of the heat.

In the face of such inconveniences, the question arose, is it not possible in spite of the poor thermal conductivity of rubber to obtain uniform heating, that is to say, for the temperature to be the same at all times at all points in the rubber? This would permit, on the one hand, a better yield from the equipment and, on the other hand, the utmost advantage to be taken of the excellent properties of the rapidly cured products which are so familiar today.

It is known that a mass of metal placed in an alternating magnetic field, for example, the iron core of a coil through which an alternating current is passed, is the seat of induction phenomena and hysteresis, which heat it rapidly, and it is also known that divisions, *e. g.*, the laminations of the core, diminish the heating without however nullifying it. It should be mentioned also that, all things being equal, this heating increases very rapidly with increase in the frequency of the current.

Accordingly one method suggests itself, namely, to disperse in the rubber conducting substances such as metallic filings, and to place the mixture in an alternating magnetic field, in short, in an induction furnace where the particles would be heated as a result of Foucault currents induced in each one. In this way hot points, sufficiently numerous to give practically uniform heating, would be distributed throughout the mass. In theory, this is very simple, but in practice there are numerous difficulties.

In the first place, at ordinary frequencies of 50–52 cycles per second, a solid core placed in a self-inductance heats quickly, whereas a laminated core heats very little. It is necessary therefore to distribute in the rubber large granular conductors in order to obtain an appreciable effect. This process is successful, but it is without practical interest.

The writer's attention was then directed to high frequency industrial furnaces invented and constructed since 1920 by René Dufour. Their frequency of 20 to 30,000 cycles per second makes it possible to use particles from 0.3 to 0.5 millimeters, or relatively fine filings. The addition of ten per cent by weight increases the temperature several degrees per minute, which is acceptable, but since the metallic mass is relatively small, the thermal yield of the system is low.

In order to improve this condition, an attempt was made to increase the proportion of granules. Unfortunately, with an increase in yield, complex phenomena appeared, and the temperature at the surface was higher than that at the center. In a cylindrical mass 20 centimeters in diameter, the temperature of the surface reached 140°C ., whereas that at the center barely exceeded 130°C . This is of course better than the older methods, but it is still unsatisfactory.

Moreover, the presence of filings makes the rubber heavy and alters its properties. It was thought that lamp black or carbon black, which are normal components of rubber mixtures, might become heated also, but unfortunately at frequencies of

20,000 to 30,000, the heating effect, though not zero, is practically negligible, so that the process under consideration is very limited in its application.

In view of the fact that the yields of induction furnaces increase with the frequency, in fact much more rapidly than the latter, the study of higher frequencies was about to be undertaken in the hope of heating the mixtures loaded with black sufficiently when, upon the advice of René Dufour, who wished to carry out the electrical portion of these investigations, an attempt was made to make use of other phenomena. If as a matter of fact a piece of paraffin is placed in an alternating electric field such as exists between the plates of a condenser supplied by a high frequency current there is rapid heating of the dielectric, which soon melts. The phenomena involved are known as dielectric viscosity and dielectric hysteresis. They are, however, more valuable in the present problem because they pass into the molecule itself, assuring absolutely uniform heating, provided the electric field is uniform. They vary with different factors, among which the most important are

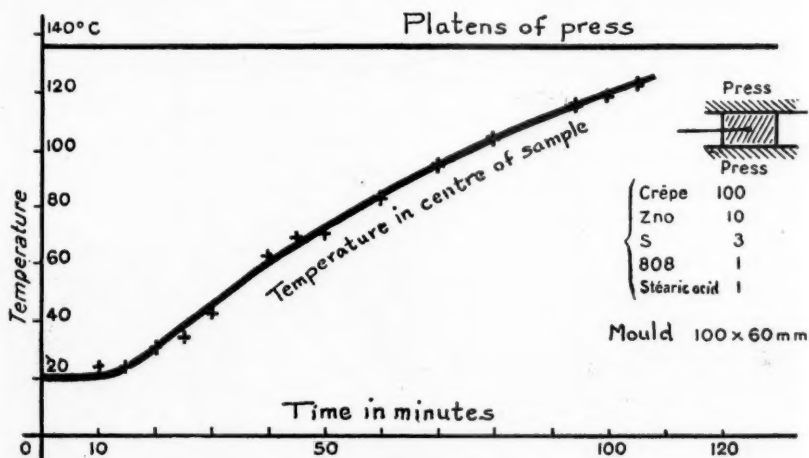


Figure 1

the nature of the dielectric, the intensity of the electric field, and the frequency of the electric field.

It should be mentioned that with high enough frequencies almost all insulators heat considerably. This offers great possibilities. Crepe heats but little, whereas a mixture with five per cent of zinc oxide and three per cent of sulfur heats very rapidly in an electric field, the frequency of which corresponds to wave-lengths of 20 to 30 meters, or a frequency of 15 to 10 millions. This value is really not at all unusual, since many radio transmitters regularly emit wave-lengths of about 20 meters, which is equivalent to a frequency of 15 millions. The power of these transmitters ordinarily reaches 50 kilowatts, *i. e.*, greater than the requirements of rubber technologists.

The results reported here were obtained with apparatus of the Compagnie française de Radiologie, and it should be mentioned that during the course of numerous experiments there was no trouble with the apparatus, and not even one fuse was blown. The manipulation of the oscillator is so simple that it requires no experience, and if these points seem to be particularly emphasized, it is because

of a desire to prove that this is not a laboratory procedure but offers commercial possibilities. The apparatus is already in existence, it is very reliable, and it is for us to make use of it.

Figures 2 and 3 represent variations of a single assembly. The two triode lamps, identical with those in radio receivers, are mounted in oscillators on a circuit formed by the self-inductances *S* and by the condenser *C*, between the plates of which the rubber to be treated is placed.

Figure 4 shows a very large dismountable triode lamp of the Compagnie Générale de Radiologie. These lamps are very economical, since when the filament has given out, only fifteen minutes is necessary to open the apparatus, to replace the filament,

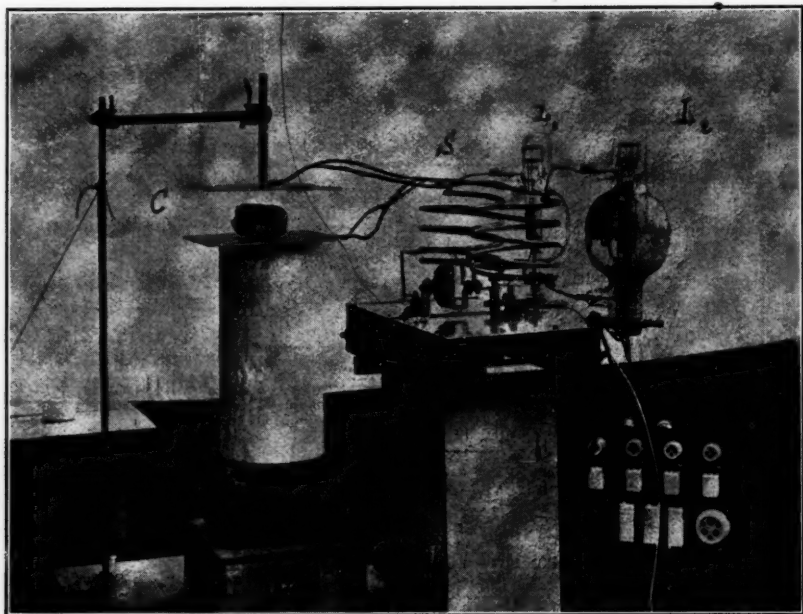


Figure 2—Experimental High Frequency Transmitter, 2 Kilowatts Power and Wave Length of 20-25 Meters

*L*₁ and *L*₂, triode lamps; *S*, self-inductance; *C*, capacity (between the plates of the condenser a sample in process of sponging is visible).

and to start again, whereas the life of ordinary lamps is limited strictly to that of the filament.

The vacuum is maintained constant in the lamp by means of a device with an automatic relay pump, thus assuring a high degree of regularity in the characteristics of the lamp.

To show the practical results obtainable let the mixture above:

Crepe	100
Zinc oxide	10
Sulfur	3
Stearic acid	1
Accelerator "808"	1

be placed between the condenser plates. In fifteen minutes a temperature of 135° C.

is reached in every part of the mass, which means for each molecule, and if this temperature is used for the cure, the power sent to the condenser can be reduced by intermittent supply, *i. e.*, one minute of heating followed by two minutes with the power off, then another minute of heating until the cure is completed. It is evident that, when the temperature of cure is reached, it is necessary only to compensate the losses of heat, which are relatively small in an apparatus that is properly heat-insulated.

In the example chosen, the total length of cure was 30 to 35 minutes, divided into a preliminary heating of 15 minutes and a cure of 15 to 20 minutes, of which only 5 minutes involved operation of the apparatus, that is, expense, since the

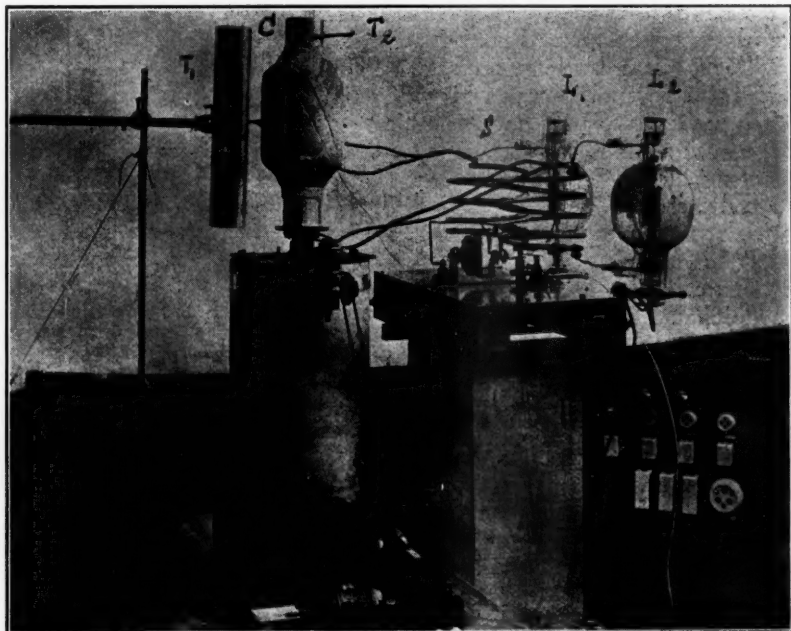


Figure 3—Vulcanization in Wrapped Form, and with a Rotary Electrode (the Electric Field Is Set Up between the Two Metal Tubes T_1 and T_2 ; the Rotation of T_2 Brings Each Point of the Rubber in Turn into the Electric Field)

process was carried out intermittently, *viz.*, 1 minute of heating, 2 minutes with the power shut off, etc.

Referring now to the temperature curve for the interior of the mass heated under pressure, which was described earlier, it will be seen that after 35 minutes of cure the temperature at the center of the piece was scarcely 50°C .

As can be seen, this method is already a step forward, but instead of using a moderately active accelerator it is really better, and it would involve no difficulty, to replace accelerator "808" by a combination which gives a suitable cure in 10 minutes. Now it will require 15 minutes to bring the sample to the temperature of cure, and then will require a little less than 10 minutes, or a total of 25 minutes, to cure a mass of rubber of any size. This is certainly a rapid process.

Here is further proof of the time to be saved by uniform vulcanization with

high frequency currents. A sponge rubber mixture was divided into two parts; one was cured by the ordinary method, the other by high frequency. The cure of the first required more than 200 minutes, that of the second was completed in 35 minutes, in spite of its being the same mixture.

To illustrate the possibilities of this method in the case of sponge rubber, a small sample was cured in the open air, without any insulation, and it was found that a raised zone at the center was correctly vulcanized, surrounded by a region

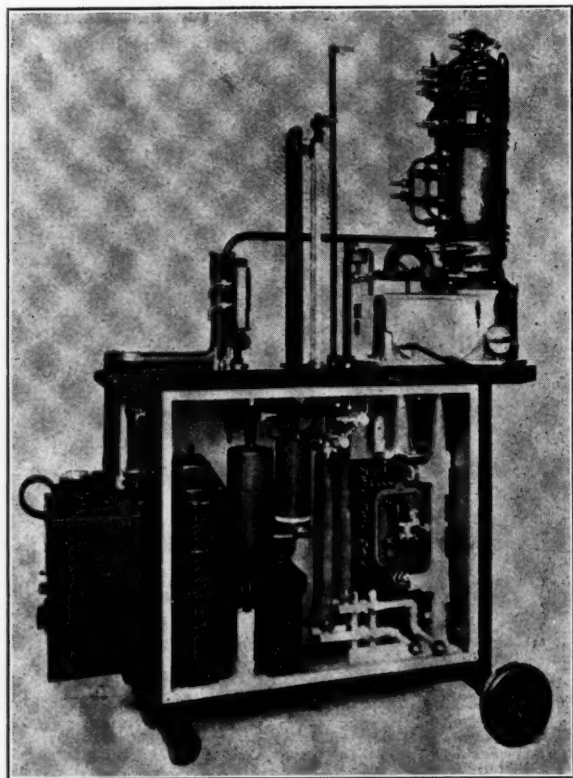


Figure 4—Dismountable Triode Lamp of High Power of the Compagnie Generale de Radiologie, Paris

less and less cured, while the surface constantly cooled by air remained completely raw.

Another curious experiment may be described. A cylindrically shaped sample of any mixture is carefully wrapped, surrounded by insulation, and suspended by a string 5 centimeters from each of two electrodes. The current is turned on and some minutes later the mixture is found to be cured, having been in contact only with cold insulation and a thread.

It has been impossible up to now to obtain such a result with any other method. The composition of mixtures plainly influences their heating and, without

entering into details, it may be mentioned that sulfur, zinc sulfide, and other ingredients increase the rate of heating of rubber.

From this point of view it is to be feared that another chapter has been added to the problems of rubber technologists for, in order to carry out uniform vulcanization it will be necessary to study how to heat the different parts of an object to be cured.

Thus in a tire, it will be necessary to adjust not only the acceleration of the different parts (tread, side wall, friction, etc.), but also their rate of heating.

Practical Results

In this still unfamiliar subject advance must be cautious, many experiments remain to be carried out, and many measurements must be made before advantage can be taken of all the possibilities which this process offers. Nevertheless there are certain results which may be considered as already achieved, *e. g.*, the curing of sponge rubber in all its forms with a uniformity and a facility of sponging and of molding which is absolutely astonishing. It is probable that any mixture whatsoever will swell with the greatest ease, and all the artifices, all the care, and, it might almost be said the acrobatics, to which recourse has been had to obtain sponge rubber belong in the past from now on.

Certainly the time of cure of any mass, no matter how large it is, can be accomplished in minutes, whereas the former methods required hours.

The equipment is the simplest; the mass to be vulcanized is placed in an insulated chamber, the form and dimensions of which are almost those of the product which it is desired to obtain. The container is placed between the electrodes of a condenser through which it is only necessary to pass high frequency currents. The operation is controlled by a watch and a wattmeter.

The same apparatus can evidently be adapted to the vulcanization of molded articles. In many cases the mold can serve as the electrode.

Another result attained is the vulcanization of sheet rubbers, flooring, and belts of great length. These sheets are rolled on a metal drum, with cloth between, and are then tightly wrapped. The drum is then surrounded by a thin sheet of metal, wound up on itself in the form of a cylinder concentric with the drum. In this way, the material to be cured is in the interior of an annular condenser, the electrodes of which are the drum on the one hand and the sheet of aluminum on the other. The only thing left to do is to pass the current.

Another extremely important application of the annular condenser is the vulcanization of linings or coverings for metal drums. In fact various industries utilize solid iron or steel drums covered with a layer of rubber, which may be as thick as 6 to 8 centimeters.

Until now, these coverings have been cured in an autoclave, but as the mass of metal is insulated by the rubber, it can only be heated at the ends, *i. e.*, slowly.

The adherence of rubber to metal is almost always effected by a layer of ebonite, and this ebonite, which requires the longest cure, is in the very coldest location. The process is endless, and almost always unsatisfactory because of the uneven cure. A mixture 5 centimeters thick heated on one surface by live steam requires four to five hours to reach 130° C. on the opposite surface. If this side is further cooled by contact with a mass of metal, the final effect may be imagined. Here is a remarkable application of high frequency currents for curing, and the advantages of the two processes which have been discussed can be combined.

The iron core is first heated by induction (high or low frequency) until the temperature is sufficiently high, for example, 120° C., which is accomplished in a few minutes. The mass is then placed inside a thin sheet of metal, rolled into the

form of a cylinder, and is concentric with the object which is being cured. In this way an annular condenser is formed, so that it is only necessary to pass a high frequency current for 30 or 40 minutes. Thus it becomes possible in this industry to utilize mixtures with rapid rates of curing and with mechanical properties and aging infinitely superior to those found at the present time.

Another interesting application would be the vulcanization of solid tires, which is a problem similar to the one just described. The metal in the tire forms one plate of the condenser, the mold or a sheet of metal represents the second plate, and vulcanization can be effected very quickly.

A final use of this form of condenser remains to be mentioned, *viz.*, the continuous curing of cables and electric wires, in which case they are led into the interior of a cylindrical electrode, the other armature of the condenser being represented by the wire itself.

Latex can be utilized advantageously in the new process, the adaptability of which is so great. It has been found possible to vulcanize latex mixtures to be used in the manufacture of sponge products by subjecting them to the action of a high frequency field, and in this case drying takes place during vulcanization.

Numerous other applications which cannot be detailed here suggest themselves. The aim has been to show the adaptability and the future of high frequency, which appears to be of extremely general application.

Efficiency

The process is far from expensive. In a recent test, 5 kilograms of rubber were vulcanized with a total energy which would have hardly sufficed to raise the same weight of water from 20° to 100° C., roughly 60 per cent.

Finally, at the Exposition de la France d'Outre-Mer held at the Grand Palais from November 28 to December 15, 1935, this apparatus was to be seen in operation at the exhibit of the Office des Inventions.

In closing, thanks are due the Syndicat du Caoutchouc, which, by giving the author one of its prizes in 1935, encouraged him to continue his investigations.

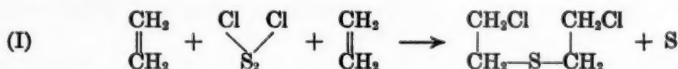
Contribution to the Study of the Vulcanization Reaction

Kurt H. Meyer and W. Hohenemser

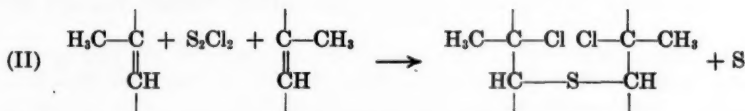
LABORATORY OF INORGANIC AND ORGANIC CHEMISTRY OF THE UNIVERSITY OF GENEVA, SWITZERLAND

In spite of the great technical importance of vulcanization, the chemical reaction involved is not yet entirely understood, although at the present time it is assumed that chemical phenomena take part in this operation. To C. O. Weber¹ in particular is due much of the research in the field of rubber. It was he who proved the chemical combination with sulfur. He assumed that during hot vulcanization, sulfur combines with two polyprene chains and that they unite chemically, but he was not able to go into this subject in more detail or to prove anything further.

The process of cold vulcanization is better understood. There are good reasons for assuming that sulfur chloride reacts with the double bond of polyprene chains in the same way that it does with olefins of low molecular weight, for example with ethylene. It is known that sulfur chloride unites with this latter according to the following scheme:



Several years ago Meyer and Mark² proved that cold vulcanization proceeds according to the same scheme:



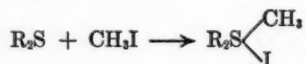
and as a result, that a bridge is formed between two polyprene chains.

In the present work, tests with cold vulcanized rubber will first be described, tests which confirm this concept of the mechanism of cold vulcanization. There is next described a *reaction for the determination of bridge linkages*, the sulfur in vulcanized rubber being united as in a thioether (C—S—C). In the second part of this work experiments will be reported which deal with the *action of sulfur on olefins* of low molecular weights under the same conditions of hot vulcanization. The reactions described here may be considered as the prototype of hot vulcanization, just as the reaction between ethylene and sulfur chloride constitutes a model for cold vulcanization.

1. If cold vulcanization proceeds according to Equation II, free sulfur should be found in the vulcanized product. In fact, we have proved that after cold vulcanization one-half of the sulfur can be extracted by sodium sulfite, but it is not soluble in acetone or in carbon disulfide. The sulfur liberated during cold vulcanization is therefore amorphous sulfur.

For the *determination of the thioether linkage* (C—S—C group) in rubber, methyl iodide was used.

It is known that dialkyl sulfides give by the addition of methyl iodide the corresponding tertiary sulfonium iodides:



Methyl iodide is easily incorporated with rubber and, according to our observations, can be separated easily again from the unvulcanized rubber. Under the same conditions the mercaptan group is not attacked by methyl iodide.

The methyl iodide index of rubber is a direct measure of the sulfur in the thioether linkage, and may even serve for a study of the progress of vulcanization.

In rubber vulcanized in the cold and containing 2.5 per cent of combined sulfur, there was found, after the addition of methyl iodide, 4 per cent of combined iodine, which corresponds to a little more than 1 per cent of sulfur combined in the state of sulfide.

Rubber with 8 per cent of sulfur, but no accelerator, vulcanized hot for three hours, absorbed 11 per cent of methyl iodide, which corresponds to a content of 3 per cent of sulfur, combined in the state of sulfide. The same sample vulcanized for 4 hours contained 4 per cent of sulfur combined as sulfide. These results prove the presence of sulfur bound in the form of a thioether linkage. For every 80 atoms of carbon, one of these linkages was found.

2. Since the thioether linkage was found in hot vulcanized rubber, it may be asked by what mechanism this reaction takes place. As it is impossible to isolate reaction products which can be analyzed, the reaction of sulfur with olefins under the conditions of hot vulcanization was studied as a model.

In the literature the following information was found relative to this reaction of sulfur with olefins.

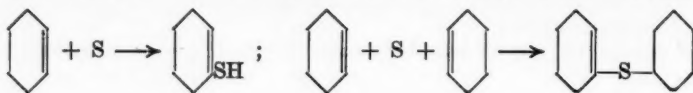
According to Baumann and Fromm³ stilbene fused with sulfur gives thionessal and hydrogen sulfide. This reaction evidently cannot serve as a model, since during vulcanization this characteristic evolution of hydrogen sulfide does not take place.

Later the same authors found that styrene when brought to the boiling point with sulfur (around 200°) gives diphenylthiophene, and at the same time some ethylbenzene. In the same reaction Michel⁴ noted the formation of an oil with the composition of C_8H_8S .

Very much later Friedmann⁵ studied the action of sulfur on aliphatic olefins under pressure in order to obtain information about the formation of sulfurated petroleum products. He obtained with β -hexylene a combination which he regarded as one of the possible mercaptans, $C_6H_{11}SH$, then a thioether, $(C_6H_{12})_2S$, and finally the substance $C_{12}H_{24}S_2$.

As a beginning, we chose cyclohexene as a model, and we studied its reaction with sulfur at a temperature of 140° to 150° C. because ethylene does not react with sulfur at 140° C.

Approximately two-thirds of the cyclohexene reacted, and gave almost equal proportions of cyclohexylic mercaptan and dicyclohexylic sulfide. The residue was composed of oils containing sulfur and having high boiling points. Besides sulfuration, there is then a reduction, which must be at the expense of a portion of the substance present. Probably unsaturated products are first formed:



which absorb hydrogen during the reaction. The hydrogen is probably furnished by the mercaptan, which gives up hydrogen by transformation to the disulfide, which then undergoes secondary transformations.

During the reaction with styrene, which we studied subsequently, we were able to obtain only the diphenylthiophene described by Baumann and Fromm. Consequently it may be assumed that substances analogous to thiophene appear just as in the reaction with cyclohexene, and that the hydrogen liberated during their formation also contributes to the hydrogenation of other products of the reaction.

The reactions studied are appreciably accelerated by the accelerators of vulcanization.

These results, in relation to the existence of sulfur in the thioether linkage in vulcanized rubber, lead to the conclusion that during hot vulcanization analogous reactions take place. It may be assumed then that a part of the sulfur combines with the polyprene chains by a thioether linkage, and that another part combines in the form of a C—S—H group. The adjacent double bonds are hydrogenated at the same time. These reactions therefore consume the hydrogen furnished by other reactions which are more complicated.

It thus becomes certain that in the two types of vulcanization thioether linkages are formed, and these unite the polyprene chains.

According to Bruni⁶ a minimal proportion of one atom of sulfur for 1500 atoms of carbon is required to obtain an appreciable vulcanization. Since the rubber chains are composed of at least 1000 atoms of carbon, there is on the average one atom of sulfur, or two bridge linkages, for each chain. In reality, the reaction is evidently much more irregular. In a rubber so little vulcanized, many chains are still independent, whereas others have three bonds for the sulfur, or even more.

If these results are considered from the morphological point of view, as Meyer and Mark⁷ did seven years ago and Hoch⁸ in a similar manner, a clear picture of vulcanization can be obtained. The long chains of the molecules which compose unvulcanized rubber, and which can be separated from one another by solvents, are united in a network of loose meshes. The diminution in plasticity and consequent stability of form, the cessation of flow, and the final formation of ebonite, by further addition of sulfur, are thus explained in a simple manner.

Experimental Part

Cold Vulcanization.—Over crepe, previously cut up into fine pieces, dry air and air saturated with sulfur chloride vapor were passed, and the excess of the latter was removed by a stream of air. The increase in weight was 9 per cent, the sulfur content 4.8 per cent and the chlorine content 4.2 per cent (Carius method).

Determination of Free Sulfur.—To determine the free sulfur, the reaction product was extracted in a Soxhlet apparatus for one day, first with carbon disulfide, then with acetone without the sulfur going into solution. On the contrary, about one-half of the sulfur passed into solution when the product was heated for two hours in a 5 per cent solution of sodium sulfite. The sulfur content after this extraction was 2.5 per cent.

Determination of the C—S—C Groups.—The rubber was let stand three days in darkness in contact with an excess of methyl iodide, was then evaporated in a vacuum and washed thoroughly several times with petroleum ether. It then showed an iodine content of 4 per cent, corresponding to 1 per cent of sulfur in the C—S—C bonds.

Control Test.—Unvulcanized rubber left in contact with methyl iodide several days, then evaporated, and washed thoroughly with petroleum ether, contained no iodine.

Determination of the C—S—C Group in Hot-vulcanized Rubber.—Rubber which had been vulcanized three hours at 147° C. with 8 parts of sulfur per 100 parts of rubber⁹ was cut up into the smallest possible pieces, and left two days in contact with an equal quantity of methyl iodide. The greater part of the latter was then removed in a vacuum, and the remainder as well as the small quantity of iodine which had formed during the contact with petroleum ether was removed by digestion in petroleum ether with renewal of this solvent. The rubber, dried to constant weight, then contained 12 per cent of iodine, corresponding to 3 per cent of sulfur combined as sulfide.

Another rubber, vulcanized four hours at the same temperature contained, after identical treatment with methyl iodide, 14 per cent of iodine, corresponding to 3.5 per cent of sulfur.

The Action of Sulfur on Ethylene.—A slow current of ethylene was passed through fused sulfur maintained at a temperature of 150° C. for several hours. The ethylene was then passed into a refrigerant maintained at -70° C., in which there was no condensation. Accordingly no reaction took place.

The Action of Sulfur on Cyclohexene.—Forty-two grams of cyclohexene, carefully fractionated to free it from the peroxide, which is frequently mixed with old cyclohexene or cyclohexene of ordinary quality, were heated in a closed tube with 6.4 grams of sulfur for five hours at 150° C. A rocking electric oven was used for this heating. The contents of several tubes were combined, and the uncombined cyclohexene was driven off. This was around 50 per cent of the quantity used.

Cyclohexyl mercaptan.—A preliminary experiment having shown the presence of an oil soluble in alkalis, the product was diluted with its volume of ether, shaken several times with dilute sodium hydroxide, acidified, the oil which separated dissolved in ether, and after drying over calcium chloride and after elimination of the ether in a vacuum, distilled. The oil which boiled between 38° and 39° C. in a vacuum of 12 millimeters was cyclohexyl mercaptan, combined with small quantities of a substance rich in sulfur.

Yield: 6 grams per 42 grams of cyclohexene

$C_6H_{11}S$	Calcd.	C 62.07	H 10.34	S 27.5%
	Found	C 62.39	H 9.85	S 28.7%

Cyclohexane-thiol, $C_6H_{11}SH$, which has been described¹⁰ with the properties of a liquid, a disagreeable aliacious odor, b. p. 150–152° C. at 155 millimeters pressure, soluble in alcohol, ether, chloroform, benzene, dilute alkalis, insoluble in water, agrees well with our product.

Cyclohexyl-o, p-dinitrophenyl Sulfide.—In order to characterize this compound, according to the method of Bost, Turner, and Norton,¹¹ this mercaptan dissolved in alcohol was treated at the boiling point in a reflux with dinitrochlorobenzene and sodium acetate. An abundance of yellow crystals separated, which after recrystallization in alcohol, melted at 147° C. They were soluble in chloroform and benzene, and were reprecipitated as pale yellow crystals from this solvent by ligroin.

$C_{12}H_{14}N_2SO_4$	Calcd.	C 51.06	H 4.96	S 11.35	N 9.93%
	Found	C 51.34	H 4.77	S 11.39	N 9.99%

Dicyclohexyl Sulfide.—The oil remaining after removal of the mercaptan was distilled in a vacuum. About one-half passed over at 130–132° C. under 11 millimeters pressure, and this was distilled again, dissolved in a very small quantity of dry ether, and cooled in a mixture of carbon dioxide and ether. The crystals which separated abundantly melted at -8° C.

Yield: 10 grams per 80 grams of cyclohexene

Calcd.	C 72.73	H 11.11	S 16.16%
Found	C 72.73	H 10.91	S 16.02%

A substance having the formula $(C_6H_{11})_2S$ has been mentioned in the literature,^{12,13} without more exact information. Our substance is liquid at ordinary temperature, colorless with a somewhat faint odor. It is insoluble in water, but is soluble in alcohol, ether, petroleum ether, acetone, benzene, carbon disulfide, carbon tetrachloride, and chloroform. Dissolved in concentrated sulfuric acid it gives an orange-red color. When pure it does not react with bromine dissolved in chloroform, while the crude product before having been crystallized absorbs small quantities of bromine. This proves that it contains at least traces of an unsaturated sulfide.

From the oil remaining after distillation of the dicyclohexyl sulfide, we were not able to isolate any clearly defined product.

Methyldicyclohexylsulfonium Iodide.—In the presence of one another, dicyclohexyl sulfide and methyl iodide rapidly form a crystalline mass, which when recrystallized in ether-alcohol gives colorless needles which melt at 110.5° C.

$C_{12}H_{24}SI$	Calcd.	I 37.35	Found	I 37.50%
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Action of Sulfur on the Styrene, 2,4-diphenylthiophene.—After heating the styrene at its boiling point in the presence of sulfur for several hours, there separate out upon cooling colorless platelets which melt $-119-20^\circ$ C. (after recrystallization from methyl alcohol). Baumann and Fromm give a melting point of 119° C. for 2,4-diphenylthiophene, which is the compound in question.

$C_{16}H_{12}S$	Calcd.	C 81.36	H 5.08	S 13.56%
	Found	C 81.21	H 5.10	S 13.40%

The Action of S on Triphenylethylene.—The triphenylethylene was first heated for seven hours at $140-150^\circ$ C. with an equimolar quantity of sulfur, then refluxed at 180° C. for four hours longer. A little hydrogen sulfide was formed, to be sure, but the principal mass of triphenylethylene could be recovered by alcohol without having undergone any transformation.

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- ⁸ Hock, See Fromandi, *Kautschuk*, **4**, 1891 (1928).
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The Influence of Mastication on the Oxido-Aging of Rubber. A Comparison with the Influence of Heating

Charles Dufraisse and Roger Vieillefosse

I. THEORETICAL PART

It may rightly be said that vulcanization improves all the properties of rubber except its tendency to deteriorate. We have undertaken a systematic study with a view to ascertaining why raw rubber, which shows so little tendency to oxidize and is so stable, loses its resistance upon being vulcanized and becomes both more easily oxidized and more easily altered. To this end, we have studied successively each of the factors which may have an influence on its oxidizability.

In a previous article¹ we settled the question of metallic impurities, particularly iron, which ordinarily is introduced into rubber either by means of the ingredients added or by removal from the steel rolls during the mechanical action. Under ordinary conditions the deleterious effect of iron, without being zero, is not great; it simply merits attention. In any case, it is not sufficient to explain the undesirable change in stability which is found after vulcanization.

Taking the factors in order, mastication was next studied.

This treatment, which is almost always necessary and the discovery of which has made possible the development of the rubber industry, would seem, *a priori*, to be rather dangerous from the point of view with which we are concerned. In the first place, it disrupts the substance, a condition which cannot be favorable to its subsequent equilibrium. But above all there is the danger that it may be an "inductor" of autooxidation.

It is known in fact that many cases of autooxidation, that of rubber among others,¹⁰ proceed extremely slowly during an initial period known as the induction period, and for a more or less long period of time the substance undergoes virtually no oxidation. This state of apparent passivity is brought to an end by contact with catalysts, among the most important of which are peroxides, including those formed during the oxidation itself; this explains the "autocatalytic" course of many autooxidations, such as that of rubber.

The investigations of Cotton¹⁰ and of Busse¹¹ have proved that mastication causes an energetic oxidation, with formation of peroxides. This is greater than is necessary to carry the mass through the zone of passivity and to establish ultimately a state of rapid oxidation.

The object of the present work was to study whether or not this is the cause of the tendency of vulcanized rubber to deteriorate.

Incidentally some experiments were carried out to establish the true effect of heating.

A. History

The first observations of any effect of milling upon the aging of rubber appear to date from 1865, when Miller¹ published some interesting results on the deteriora-

tion of rubber. A comparison between raw samples before and after milling and samples that were allowed to age naturally showed that unmilled rubber deteriorates less rapidly than milled rubber. This deterioration was attributed by Miller to the influence of oxygen and light.

Thomson² confirmed these results in 1885 by unpublished observations of Moseley, and advanced in addition the novel hypothesis of the part played by oxygen during milling. C. O. Weber³ in 1903 pointed out that the oxidizability increases with the time of milling.

Ahrens⁴ in 1910 emphasized the deleterious effect of overmastication. A little later⁵ he assumed that the particles of rubber are covered with an oxidized film, supposed to be a protection against subsequent alteration. By destroying this film, mastication makes the rubber oxidizable.

Gorter⁶ in 1912, King⁷ in 1922, Leon and Lister⁸ in 1927, and Kohman⁹ in 1929 successively called attention to the great tendency of overmasticated rubber to oxidize (see also van Rossem⁸).

Finally in work on various industrial mixtures, Wiegand¹³ in 1932 reported that there is a diminution in the resistance to aging when rubber is masticated excessively, particularly when milled hot and when accelerators are present.

On the other hand, Porritt¹⁷ in 1921 found that mastication increases the stability toward light.

B. Technic of Milling

The milling tests in the case of pure rubber or simple mixtures, *i. e.*, rubber and sulfur, were carried out on a laboratory mill, and in the case of commercial mixtures, on a factory mill. The total mechanical work to which the mass of rubber was subjected was evaluated both by the time of milling and, more important, by the lowering of the viscosity of its benzene solutions.²⁰

During these numerous experiments we had an opportunity to observe the different and now classic phenomena of the production of static electricity and of the occlusion of gaseous particles in rubber.

In particular, a sample of excessively milled rubber when placed in a vacuum had a tendency to acquire a spongy structure temporarily, as a result of the expansion of the gas contained within the mass.

C. The Initial Oxidizability of Raw Rubber of Different Types

Technologists have known for a long time that the properties of rubber vary enormously with its origin. For this reason, we determined the initial oxidizability of different types of commercial rubber. Those utilized in this investigation were pale crepe, sheet Para, and smoked sheet; others such as "sprayed" latex, coagulated latex, and Congo are considered here only for purposes of comparison.

Figure 1 represents the results of the tests at 80° C. In order of increasing oxidizability they are pale crepe, washed Para, smoked sheet, sprayed latex, coagulated latex, and Congo.

The first three samples showed only slight differences, whereas the others, in particular Congo, proved to be more readily oxidizable.

D. The Influence of Mastication on the Oxidizability of Raw Rubber

1. *Rubber Alone.*—These tests were carried out on pale crepe, smoked sheet, ball Para, and coagulated latex.

(a). *Pale Crepe.*—Pale crepe was worked for a long time on a laboratory mill,

and samples were removed periodically. The viscosity of each sample in benzene was determined, to follow the progress of the mechanical working.

The oxidizability increased fairly regularly in proportion to the mechanical work (Fig. 2). However, even as extensive mastication as that of the fourth sample gave an increase in oxidizability of only three to four times that of the sample which was milled the least. This increase is certainly small if it is compared with the difference in oxidizability which distinguishes raw rubber from vulcanized rubber (50 to 100 times).

(b). *Smoked Sheet*.—The same test, carried out on smoked sheet, gave a comparable result, that is a three-fold increase in oxidizability after very extensive mechanical working (Fig. 3).

(c). *Ball Para*.—With ball Para which received the same treatment as pale crepe and smoked sheet, there was an increase in oxidizability with the time of milling.

However, the sample gave an oxidizability curve which was abnormal at the beginning, with the equally abnormal formation of moisture, which condensed in the

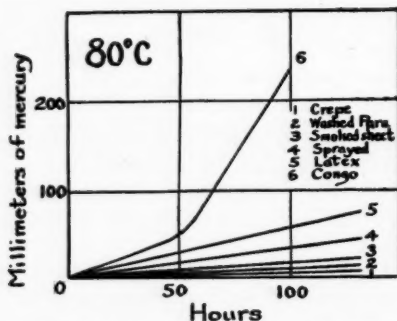


Figure 1—Comparative Tendencies of Various Types of Rubber to Oxidize

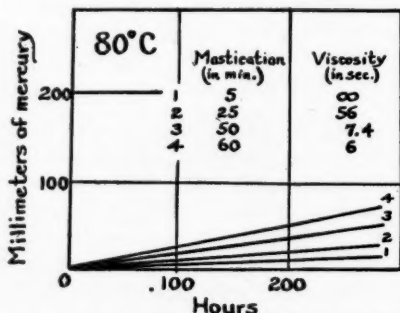


Figure 2—Influence of Mastication on the Oxidizability of Raw Crepe

manometric tube. Since the milled samples no longer showed this phenomenon, it might be thought that crude ball Para contained traces of a very easily oxidized substance which is oxidized and destroyed at the beginning of milling.

Whatever may be the cause of this anomaly, a four-fold increase in oxidizability was observed with more extensive milling (Fig. 4).

(d). *Latex*.—A coagulated latex (Jatex) prepared by precipitation with calcium chloride, and then washed and dried, was milled, with the removal of samples periodically.

Figure 5 shows after extensive milling a coefficient of increase at least five times that of the original sample, this latter behaving rather poorly.

II. INDUSTRIAL MIXTURES

There was no point in testing commercial mixtures in the raw state, because such mixtures do not ordinarily remain in this state. It was however instructive to see if mastication played any part in their tendency to oxidize, as it did with rubber alone.

Two formulas were used in this investigation. The first contained diphenylguanidine, the second tetramethylthiuram disulfide. In this way two different types of accelerator were used, one a moderate accelerator and the other an ultra-

accelerator. Naturally in this case, mechanical treatment did not vary within such large limits as with pure rubber, since the completion of a homogeneous mixture presupposes a preliminary mixing.

(a). *Mixtures with Diphenylguanidine.*—In the first test three mixtures of the same formula were prepared successively on a laboratory mill, except that the rubber was milled for longer and longer periods, viz., 18 minutes for the first, 26 minutes

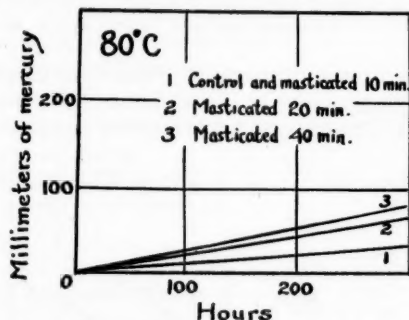


Figure 3—Influence of Mastication on the Oxidizability of Raw Smoked Sheet

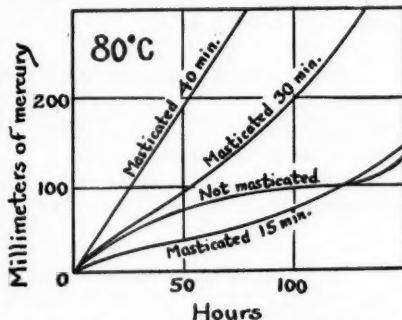


Figure 4—Influence of Mastication on the Oxidizability of Unwashed Ball Para Rubber

for the second, and 40 minutes for the third. In this way the samples obtained when judged by the external appearance, were undermasticated, normally masticated, and overmasticated.

When the rubber was cold (Fig. 6), the tendency to oxidize increased only very slightly with the time of milling, the most severely milled sample being hardly 1.5 times more easily oxidized than the sample milled the least.

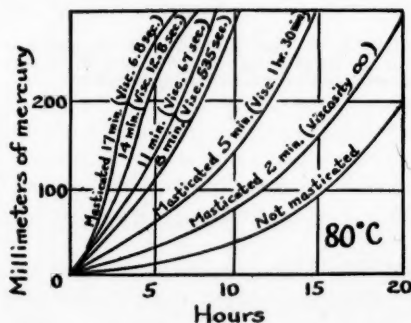


Figure 5—The Influence of Mastication on the Oxidizability of Congulated Latex (Jatex, Congulated by Calcium Chloride)

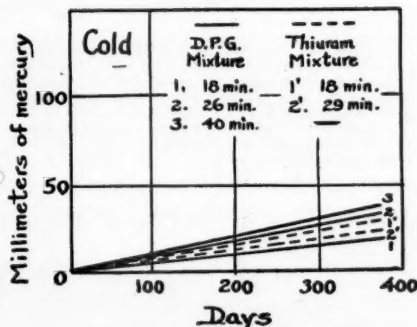


Figure 6—The Influence of Mastication on the Oxidizability of Unvulcanized Industrial Mixtures (Containing Diphenylguanidine and Tetramethylthiuram Disulfide, Respectively) When Cold

At 80° (Fig. 7), an increase with milling was no longer observed; on the contrary the least milled sample was the most easily oxidized.

A second test was made, using this time a factory mill with a capacity of ten kilograms, which yielded four portions, of which the viscosities of the benzene solutions corresponded to the following times of flow expressed in seconds: 23, 16.1, 11.6, and 9.2.

At 80° (Fig. 8) there was a slight increase in the oxidizability as milling continued. The difference between the two extremes amounted to hardly one-fourth of the average oxidizability.

(b). *Mixtures with Tetramethylthiuram Disulfide*.—Two mixtures were prepared on a laboratory mill for 18 and 20 minutes, respectively. The viscosities were not taken, but the second mixture was distinctly more plastic.

In the cold (Fig. 6), the difference in the oxidizability was negligible. It was a little more evident at 80°, the less severely masticated sample being again the more easily oxidized (Fig. 7).²¹

As in the case of the diphenylguanidine mixture, a second test was made under the same conditions on a factory mill having a capacity of 10 kilograms. Three samples were taken. The accelerator was introduced at the end of the process in order to avoid scorching.

The viscosities of the three samples corresponded to the following times of flow expressed in seconds: 31.1, 26.5, 16.8.

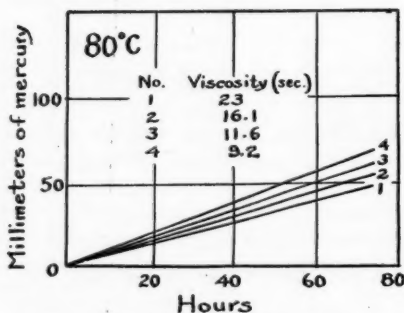


Figure 7—The Influence of Mastication on the Oxidizability at 80° C. of Unvulcanized Industrial Mixtures (Containing Diphenylguanidine and Tetramethylthiuram Disulfide, Respectively). The Rapid Ascent of the Mixture with Tetramethylthiuram Disulfide Is Attributable to Vulcanization during Heating at 80° C.

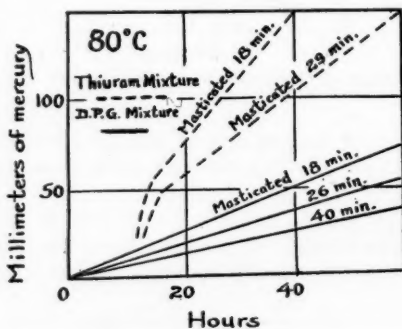


Figure 8—The Influence of Mastication on the Oxidizability at 80° C. of a Raw Mixture Containing Diphenylguanidine

The test in the cold (Fig. 9) showed a slightly greater oxidizability for the less severely masticated samples.

The test at 80° was not carried out with this mixture, because it would have been of little significance in view of the vulcanization brought about by the ultra-accelerator at this temperature.

To confine ourselves first of all to a simple examination of the oxidizability of a mixture containing an ultra-accelerator, tetramethylthiuram disulfide seemed to be practically unchanged by the extent of the mechanical treatment it received. Thus, as we have shown earlier,¹⁵ if progressive milling introduces increasing quantities of iron into the rubber, this iron is not in an active form and cannot be a factor in explaining the increase in oxidizability.

Accordingly it is to the action of mechanical work, as such, that the changes in the resistance to oxido-aging observed in the present work are to be attributed.

Briefly then, the influence of mastication on raw rubber or raw rubber mixtures varies with the conditions, is at times negligible, and is always relatively slight.

III. THE EFFECT OF EXCESSIVE MILLING

We have tried to determine if oxidizability is not considerably increased by excessive mastication.

To this end, crepe was milled until a viscous gluey mass was obtained. Four samples were taken between the point of normal milling and the end of the process. Figure 10, which shows the oxidizability of these samples, does not reveal a disproportionate increase in the oxidizability relative to the viscosity. Instead of a three-fold increase over normal mastication, excessive mastication carried to its limit gave an increase of only six-fold.

Therefore there does not seem to be any discontinuity in the action of mechanical

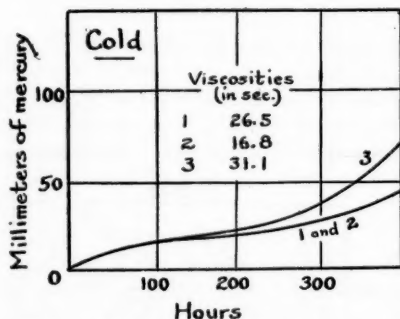


Figure 9—Influence of Mastication on the Oxidizability of an Unvulcanized Mixture Containing Tetramethylthiuram Disulfide When Cold

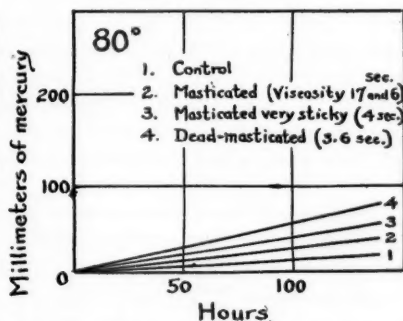


Figure 10—Influence of Excessive Mastication on the Oxidizability of Raw Crepe

work in passing from normal mastication to extreme overmastication. In any case, the oxidizability does not exceed a coefficient of six.

E. The Influence of Milling and Heating Combined

Before studying the influence of mastication after vulcanization, it was indispensable to examine, at least briefly, the changes which simple heating in the absence of sulfur might bring about in the oxidizability of milled crude rubber.

This study was not done on a sample over a range of temperatures, for it was considered sufficient to study the influence of heating at 143°C , *i. e.*, under the ordinary conditions of vulcanization. For comparison, some samples were heated at 80°C .

In addition, in order to lessen the severe effect of the oxidation phenomena, these tests were carried out *in vacuo* at a pressure of 0.01 mm. of mercury.

(a). *The Influence of Heating on Crude Rubber.*—This test was carried out on Para, crepe, smoked sheet, sprayed latex rubber, and coagulated latex, each of which was heated for four hours at 143°C . at a pressure of 0.01 mm. of mercury.

The study of the oxidizability (Fig. 11) showed that the influence of heating varied within large limits with the type of rubber, and was independent of the original oxidizability.

If the increase in oxidizability is determined, as was done in the case of milling, by comparing the times at the end of which there was the same absorption of oxygen (the same rise of mercury), the values shown in Table I are obtained.

Thus when crepe was heated four hours at 143°C ., its oxidizability increased eight times, whereas smoked sheet remained almost unchanged.

It was noted moreover (see Fig. 12) that the oxidizability of raw crepe appeared to increase slightly with the time of heating.

(b). *The Influence of Heating on the Oxidizability of Masticated Rubber.*—

TABLE I

INFLUENCE OF HEATING IN A VACUUM AT 143° C. FOR FOUR HOURS ON THE INCREASE IN OXIDIZABILITY OF VARIOUS SAMPLES OF UNMILLED RUBBER

Type of Rubber	Coefficient of Increase of Oxidizability
Crepe	8
Latex coagulum	6
Para	4
Sprayed latex	1.8
Smoked sheet	1.25

Masticated crepe, of known viscosity, was treated under the same conditions as before at 143° C. and then tested for its oxidizability.

Figure 12 shows that the relation between the oxidizability of the masticated and of the untreated crepe remained the same after heating, i. e., in the sense that there was a simple increase in the two coefficients of activity. For example,

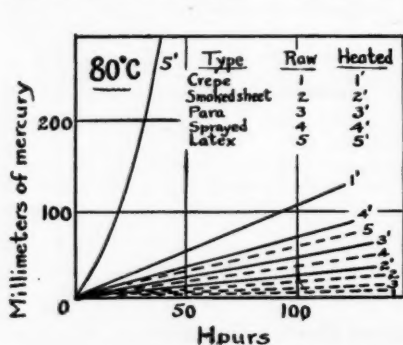


Figure 11—Influence of Heating in a Vacuum (0.01 mm. Hg.) for 4 hours at 143° on the Oxidizability of Various Types of Raw Rubber

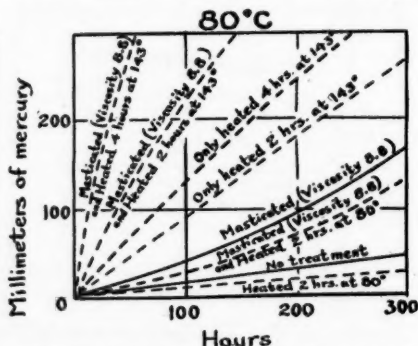


Figure 12—Simultaneous Influence of Heating in a Vacuum and of Mastication on the Oxidizability of Raw Crepe

in the case of crepe, normal mastication gave a coefficient of activity of 3, and heating (four hours at 143°) a coefficient of 8, which resulted in a final coefficient representing twenty-four times the oxidizability of the original crepe.

The interesting point of this investigation (Fig. 13) is that the effect of mastication, even when carried very far, appears to remain after heating.

Finally, heating at a moderate temperature, i. e., only 80° C., instead of decreasing the resistance to oxygen, as at 143° C., on the contrary seemed to increase it (Fig. 12, the first two broken curves at the bottom). This anomaly must be due to the destruction of the peroxides within the mass, which are, as mentioned at the beginning, catalysts of autooxidation.^{12,22} Heating would thus have two opposite results: one a rather favorable or at least not a harmful effect at slightly elevated temperature, and the other, a definitely harmful effect at 143°.

F. The Role of Mastication in the Oxidizability of Vulcanized Rubber

To obtain a more precise knowledge of the role of mastication under practical conditions, it would be necessary to obtain vulcanized samples without having to masticate them. Latex should make such a test possible, but we have not been

successful in working out a technic which will consistently give coagula from the same latex with somewhere near the same tendency to oxidize. The results, have been so uncertain that temporarily we have had to give up the use of latex. We have worked with crepe and smoked sheet, lots of which were easily obtained with a sufficiently uniform tendency to oxidize.

It would be necessary likewise to consider the influence of mastication on the optimum time of vulcanization. In the investigation of aging (see below) this was taken into account, but the effect was too slight to merit consideration under the conditions.

I. Simple Mixtures (Rubber with Six Per Cent Sulfur)

In the first series of tests, mixtures were prepared by a special method without any milling, and their tendencies to oxidize were compared with those of normally masticated samples. In a second series the tendencies to oxidize of samples which had been masticated to different degrees were compared.

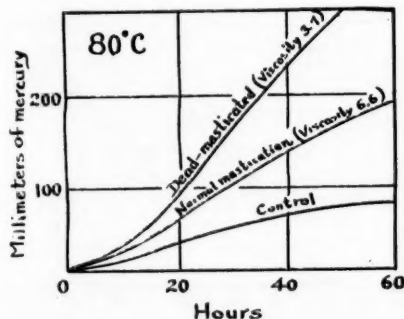


Figure 13—Simultaneous Influence of Heating in a Vacuum and of Mastication on the Oxidizability of Raw Crepe. (All the Samples Were Heated Uniformly, for 2 Hours at 80° C., Then 4 Hours More at 143° C.)

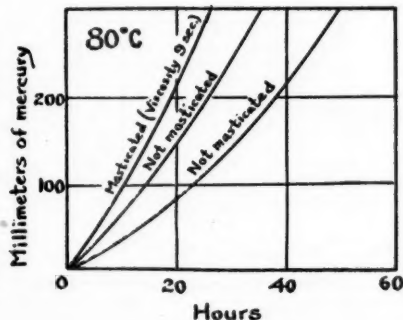


Figure 14—Influence of Mastication on the Oxidizability of Crepe Vulcanized 4 Hours at 147° C. (The Two Curves Designated "Not Masticated" Correspond to Two Parts of a Sheet Prepared by Incorporation of Sulfur in the Crepe without Mastication)

(a). *Unmilled Vulcanizates.*—A large number of rings cut from thin crepe were piled one upon the other and dusted with sulfur as uniformly as possible. The number of rings had to be large enough to assure considerable pressure between the platens of the press during vulcanization, and the total weight of the sulfur added had to be at least six per cent.

The same crepe, milled normally (viscosity: 9 seconds) and containing six per cent of sulfur was vulcanized for the same length of time, i. e., four hours at 147° C.

Vulcanization under pressure of the mass prepared in the manner described gave an excellent product, which was extremely nery, transparent, and homogeneous in appearance. However, according to Fig. 14 the homogeneity is not perfect, because an appreciable difference is evident in the oxidizability of two different parts of the same sample.

In contrast to this, mastication promoted the absorption of oxygen only slightly. According to the Graph in Fig. 14, the coefficient of increase barely exceeded two, a lower value than that observed above without vulcanization.

A second test, carried out under the same conditions, gave a similar result (Fig. 15).

Without attaching undue significance to these experiments, we can at least conclude that vulcanization has a tendency to diminish the harmful effect of milling.

(b). *Progressive Milling*.—Three unvulcanized sheets were milled for 10, 20, and 30 minutes, respectively, and were then exposed to oxidation (Fig. 16). The last two had the same tendency to oxidize, which was approximately double that of the severely masticated sheet. Accordingly vulcanization lessened the effect of milling.

II. Industrial Mixtures

Because of the lack of homogeneity of sheets prepared by our method of dusting with sulfur, only the method of progressive milling was used for industrial mixtures, the compositions being the same as for the study of the raw material.

1. *Diphenylguanidine Mixture*.—The three mixtures prepared for the experiments before vulcanization (see page 207) were vulcanized for 45 minutes at 143° C., forty-eight hours after milling.

In the cold (Fig. 17) only slight differences were observed between the three

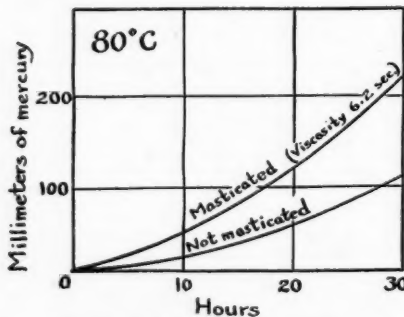


Figure 15—Influence of Mastication on the Oxidizability of Crepe Vulcanized 3.5 Hours at 147° C. (The Sample Designated "Not Masticated" Was Prepared by Incorporation of Sulfur in the Crepe without Mastication)

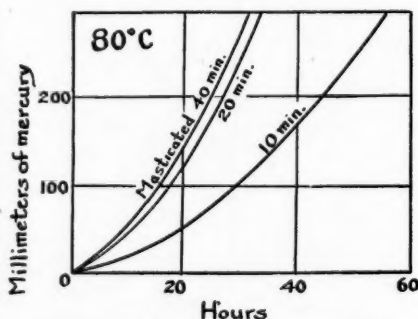


Figure 16—Influence of the Time of Mastication on the Oxidizability of Crepe Vulcanized 3.5 Hours at 147° C.

curves, the least masticated having the greatest oxidizability. This result was again found at 80° C. (Fig. 18). Moreover, the differences between the two are too small to be of any significance.

In a second test four samples were examined with viscosities corresponding to the following times of flow, expressed in seconds: 23, 16.1, 11.6, and 9.2 (see pages 207–8). In the cold (Fig. 19) the oxidizability of rings cut out for the breaking tests was not influenced by the degree of mastication. At 80° C. there was an increase in the oxidizability with the time of mechanical treatment (Fig. 20), which at its maximum reached double the original value.

2. *Mixtures with Tetramethylthiuram Disulfide*.—The two mixtures prepared for the tests before vulcanization (see page 208) were vulcanized 10 min. at 143° C.

In the cold (Fig. 17) only a slight difference was observed as milling proceeded. At 80° C., the two curves were superposed (Fig. 18).

A new experiment was carried out with three mixtures which had been masticated to an increasing extent. The viscosities corresponded to the following rates of flow expressed in seconds: 31.1, 26.5, and 16.8.

Each mixture was vulcanized for four different periods of 7, 10, 13, and 16

minutes, with a view to determining whether the optimum varied with the extent of mastication. The different vulcanizates thus obtained were oxidized.

In the cold (Figs. 21 and 22).—(1) The differences in the tendencies to oxidize of the raw samples were insignificant, as has already been seen in Curve 9.

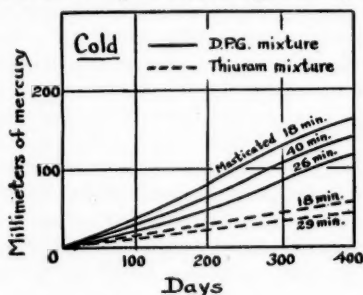


Figure 17—Influence of the Time of Mastication on the Oxidizability of Vulcanized Industrial Mixtures (Containing Diphenylguanidine and Tetramethylthiuram Disulfide, Respectively) When Cold

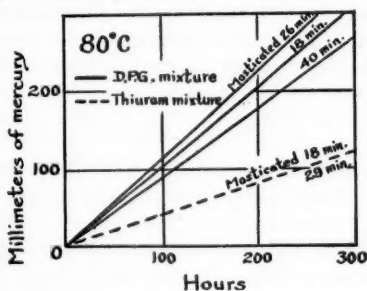


Figure 18—Influence of the Time of Mastication on the Oxidizability of Vulcanized Industrial Mixtures (Containing Diphenylguanidine and Tetramethylthiuram Disulfide, Respectively) When Hot

(2) For equal times of vulcanization no systematic change in the oxidizability with the milling was observed.

(3) For equal times of milling, an almost regular increase in oxidizability was observed with the time of vulcanization, the most highly vulcanized samples (16

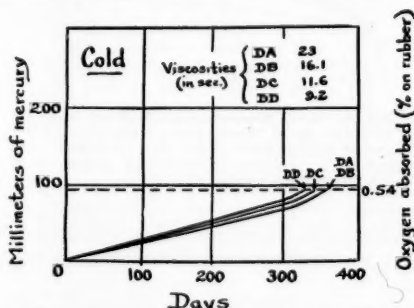


Figure 19—Influence of the Extent of Mastication on the Oxidizability of a Cold Mixture Containing Diphenylguanidine, and Cut into Rings Ready for Mechanical Tests. The Oxidation of Each Sample Was Stopped When It Had Gained 0.54% by Weight (Based on the Rubber)

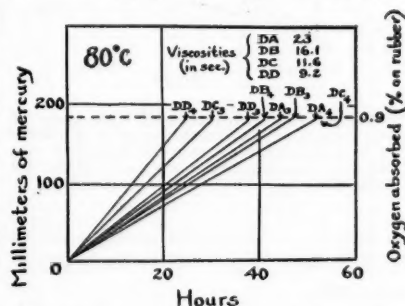


Figure 20—Influence of the Extent of Mastication on the Oxidizability, When Hot, of a Mixture Containing Diphenylguanidine, and Cut into Rings Ready for Mechanical Tests. The Oxidation of Each Sample Was Stopped When It Had Gained 0.9% by Weight (Based on the Rubber). The Subscripts 3 and 4 Serve to Differentiate the Two Samples Subjected to the Same Treatment

min.) showing practically twice the oxidizability of the least vulcanized (7 min.) samples.

In short, for industrial mixtures, as in the case of simple mixtures, vulcanization diminished the effect of mastication.

G. The Influence of Mastication on the Aging of Industrial Mixtures

There remained to be studied whether vulcanization diminishes the harmful effects of mastication on aging as it diminishes these effects on the tendency to oxidize.

Schopper rings were cut out from each of the mixtures with diphenylguanidine and tetramethylthiuram disulfide. They were then placed in flasks and were oxidized both in the cold and at 80° C. Some of the test rings were placed in a vacuum and heated the same length of time at the same temperature.

These rings were made to absorb a proportion of oxygen which was determined arbitrarily for each experiment, but below one per cent of the weight of actual rubber in the mixture; after this they were allowed to stand for 24 hours before their tensile strengths were determined.

1. Mixtures with Diphenylguanidine

These tests were carried out on mixtures DA, DB, DC, and DD, which varied only in the increasing extent of mastication (see the Experimental Part for details).

(a). *Study of the Time of Optimum Vulcanization as a Function of the Mastication.*—Two of the extreme mixtures DA and DD (viscosities corresponding, respectively, to the times of flow of 23 and 9.2 seconds) were each vulcanized for 40, 50, 60, and

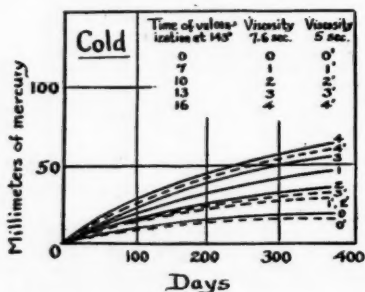


Figure 21—Simultaneous Influences of the Extent of Mastication and of the Time of Vulcanization on the Oxidizability of a Mixture Containing Tetramethylthiuram Disulfide

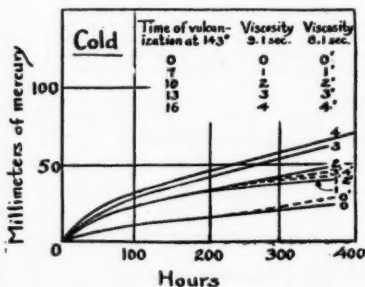


Figure 22—Simultaneous Influences of the Extent of Mastication and of the Time of Vulcanization on the Oxidizability of a Mixture Containing Tetramethylthiuram Disulfide

70 minutes. Eight test samples were thus obtained, from each of which were cut six Schopper rings. After 24 hours of rest the ordinary tensile coefficients were measured.

According to the results in Table III, condensed in Fig. 23, and contrary to what has been found under other conditions by several authors, the influence of mastication on vulcanization is not manifested in a change in the optimum times of vulcanization. It has rather the effect of shortening the period of time which is favorable to good mechanical properties. As a result, a time of vulcanization of 55 minutes was chosen for the final four test-pieces.

(b). *Oxidation.*—The test-pieces were oxidized at 80° C. and at room temperature until they had absorbed oxygen in the proportions of 0.9 per cent, based on the actual rubber, in the first case, and only 0.54 per cent in the second, in order not to prolong the experiments indefinitely (Figs. 19 and 20).

Though at 80° C., sample DA, which was milled the least, appeared a little more altered than the three others (Table IV), the difference was only slight; moreover the latter three showed virtually the same alteration, the differences observed between the two sheets of the same sample being of the same order of magnitude as those between two different mixtures.

At room temperature (Tables IV and V) the differences, otherwise slight, between

the tendencies to oxidize are irregular, and bear no simple relation to the time of milling.

II. Mixtures with Tetramethylthiuram Disulfide

The experiments were carried out on mixtures TA, TB, and TC, which differed only in the fact that they were masticated to increasing extents.

A systematic study was not made to determine whether there is any change in the optimum mechanical properties with the extent of mastication, but the preliminary experiments shown in Fig. 24 indicate that there is no notable change in the position of the optimum.

Oxidation.—The mixture was oxidized at 80° C. and at room temperature until 0.67 per cent of oxygen was absorbed by weight of the rubber in the first case, and 0.26 per cent in the second (Figs. 25 and 26).

At 80° C. (Table VI) the variation is considerable, even in the case of samples

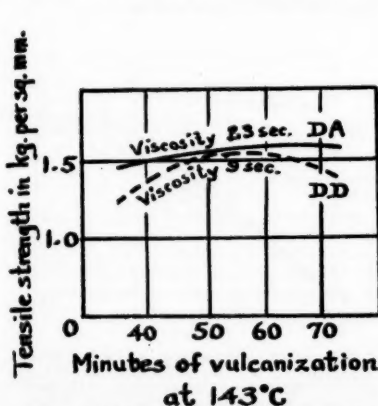


Figure 23—Determination of the Optimum State of Vulcanization of a Mixture Containing Diphenylguanidine, by the Extent of Mastication (Judged by the Viscosity of Its Solutions). The Values Correspond to Those of Table III

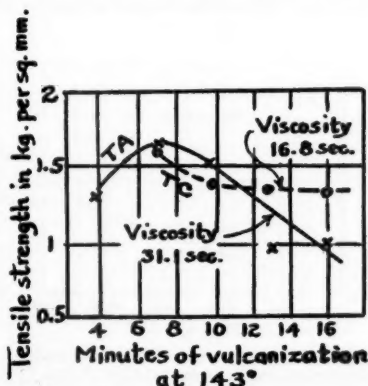


Figure 24—Determination of the Optimum State of Vulcanization of a Mixture Containing Tetramethylthiuram Disulfide by the Extent of Mastication (Judged by the Viscosity of Its Solutions). The Values Correspond to Those of Table VI

stored in a vacuum, which is attributable in all probability to undercure vulcanization of the mixtures.

No definite influence of mastication was observed.

The experiment at room temperature (Table VII) likewise showed a marked effect of mastication. Only an increase in the tensile strength was evident, *i. e.*, negative values of loss, due doubtless to a slight aftervulcanization which approached the optimum of vulcanization.

III. General Résumé and Conclusions

Without question, mastication increases the oxidizability of raw rubber. Nevertheless this influence remains slight even when mastication is carried to an excessive degree, in which case the coefficient of increase does not exceed six. In the case of a normally plasticized mixture, the oxidizability is not usually increased four-fold.

In contrast to this, heating around 140° C. has a more pronounced effect, since a coefficient of eight is easily attained at the end of four hours.

On the other hand, the two influences, that of mastication and that of heating, remain independent of each other, which results in multiplying their effects. Mastication increases the oxidizability three-fold on an average, and it is increased another eight times at least by heating which corresponds to vulcanization without an accelerator. This increase thus becomes 3×8 , or 24, a truly high coefficient.

Very fortunately, the chemical process of vulcanization has an effect opposite to that of mastication. When this chemical process has taken place, the influence of subsequent mechanical work is no longer felt except in a very diminished way.

The case does not seem to be the same with heating. However, in this case the facts are more difficult to interpret, and it is on this subject that we are now carrying out experiments.

It may simply be said that at moderate temperatures (80° C.) heating in a vacuum seems rather favorable, doubtless because it destroys the peroxides which induce oxidation. Here is a factor which merits consideration in practice.

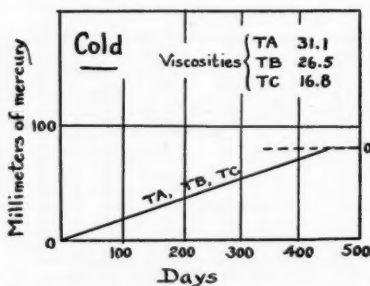


Figure 25—Influence of the Extent of Mastication on the Oxidizability, When Cold, of a Mixture Containing Tetramethylthiuram Disulfide, and Cut into Rings Preparatory to the Mechanical Tests. The Oxidation of Each Sample Was Stopped When It Had Gained 0.26% by Weight (Based on the Rubber)

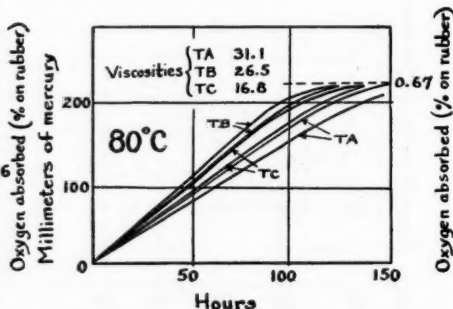


Figure 26—Influence of the Extent of Mastication on the Oxidizability, When Hot, of a Mixture Containing Tetramethylthiuram Disulfide, and Cut into Rings Preparatory to the Mechanical Tests. The Oxidation of Each Sample Was Stopped When It Had Gained 0.67% by Weight (Based on the Rubber). Each Curve Corresponds to Three Rings from Each Sample, TA, TB, and TC

In short, mastication plays only a small part in the tendency to oxidize which is shown by vulcanized rubber.

However, this operation damages the resistance to oxido-aging. It is preferable to reduce it as much as possible, and the ideal case is, from all points of view, most certainly to avoid it altogether.

It is a curious fact that vulcanization, though increasing a hundred-fold the tendency of rubber to oxidize, exerts a pronounced protective action against two factors which cause an increase in this oxidizability, viz., iron as was shown previously,¹⁵ and mastication, as is shown in the present paper. Thus it is by some peculiar action that vulcanization imparts to rubber such a marked affinity for oxygen.

PART III. EXPERIMENTAL PART

A. The Influence of Mastication on the Oxido-Aging of Raw Rubber and of Simple Vulcanized Mixtures of Rubber and Sulfur

It is not necessary to give a further explanation of the experiments on raw rubber and simple vulcanized mixtures (rubber and sulfur), because the information and the graphs which are given in the theoretical section are sufficient in themselves.

The tendencies to oxidize are of interest in most cases only for purposes of comparison, and the quantities of oxygen absorbed were determined in absolute values only in those cases where the mechanical properties after oxido-aging were measured. This will be described in the following paragraph. The constants of the pipette which was used in the comparative viscosity measurements are also given later.

B. The Influence of Mastication on the Oxido-Aging of Industrial Mixtures

As has been seen in the theoretical part, two formulas were utilized in this investigation, making use of two accelerators of different types, diphenylguanidine and tetramethylthiuram disulfide (Table II).

TABLE II

Composition of Two Individual Mixtures

Smoked sheet	55
Zinc oxide	25
Talc	12.5
Carbon black	5
Sulfur	2
Diphenylguanidine	0.5
Smoked sheet	100
Zinc oxide	40
Carbon black	20
Stearic acid	1.8
Sulfur	2.5
Tetramethylthiuram disulfide	0.35
Mercaptobenzothiazole disulfide	0.25
Commercial antioxygen	1.8

I. Mixtures with Diphenylguanidine

1. *Preparation of the Mixtures.*—In the first experiment, three mixtures corresponding to 3 periods of increasing milling were prepared on a laboratory mill 0.30 meter long and 0.20 meter in diameter. Since the capacity of such an apparatus is limited, two batches of material were milled in the same way separately, and were then rapidly combined so that a quantity of rubber sufficient for all the tests was obtained. The fillers were introduced in the usual way, the rolls being kept cold. The viscosities were not measured.

Ten kilograms of the mixture were prepared in a second experiment on a factory mill one meter in length and 0.40 meter in diameter. After the smoked sheet had been heated by several passes, the zinc oxide, talc, and carbon black were added during nine minutes, and immediately afterward the sulfur was added. Following this, the mixture was milled until homogeneous on rolls which were non-rigid, which required about 24 minutes. Three kilograms of rubber were then removed, and this represented the minimum undermasticated sample (DA). The remaining 7 kilograms were milled for 10 minutes more on set rolls, and then the entire mass was removed and 2 kilograms were taken for the second sample (DB).

In order to obtain more severe milling of the rest of the mixture, the work was continued on a laboratory mill, which, being shorter, had a smaller clearance for the rubber and assured a more severe mastication. Since the capacity of this apparatus was limited, as has already been said, the 5 kilograms were divided into 5 portions, which were milled as follows: two for 10 minutes and three for 15 minutes. They were then made homogeneous by passing the first two portions through a factory mill, making the third sample (DC), and then the last three portions, which made the fourth sample (DD), the most highly masticated one.

The four samples were cooled, and to each was added the accelerator in the form of a master batch containing 10 per cent of diphenylguanidine, according to the formula in Table II.

In short,

- 3 kg. of DA were milled 29 minutes on a factory mill.
- 2 kg. of DB were milled 37 minutes on a factory mill.
- 2 kg. of DC were milled 37 minutes on a factory mill and then 10 minutes on a laboratory mill.
- 3 kg. of DD were milled 37 minutes on a factory mill and then 15 minutes on a laboratory mill.

Examination showed mixture DA to be very nervy and distinctly less masticated than ordinary mixtures, whereas DD was soft and sticky and was distinctly over-masticated.

Viscosity.—As was pointed out at the beginning, the viscosity was evaluated by the time of flow in seconds of a solution of 1.82 grams of mixture, corresponding to 1 gram of pure rubber in 25 cubic centimeters of benzene, between the two marks of a pipette,²³ at a uniform temperature of 20° C.

The times of flow were

DA	23 seconds
DB	16.1 seconds
DC	11.6 seconds
DD	9.2 seconds

It should be said at this time that these results have only a relative value, and should not be compared to the absolute values of the viscosities of rubber alone, because of the presence of fillers which alter the viscosity in an unexplained way.

2. *Determination of the Time of Optimum Vulcanization as a Function of Mastication.*—This experiment was carried out with the most severely masticated mixture (DD) and with the least masticated mixture (DA) so that it was necessary merely to interpolate for the two others, if a displacement of the optimum was found.

Four sheets of each of the two mixtures were prepared, and were vulcanized for 40, 50, 60, and 70 minutes, respectively. Six rings were cut from each sheet and were tested on a Schopper machine. Table III and Fig. 23 show that the time of optimum vulcanization was 55 minutes.

3. *Study of Aging.*—The four mixtures, DA, DB, DC, and DD, were vulcanized for 55 minutes at 143° C., four sheets being prepared from each, which made it possible to cut six rings for the Schopper machine from each sheet.

(a). *Original Mechanical Properties.*—In order to take into account slight individual differences between the different sheets of the same mixture, two rings were cut from each of the four sheets, and were numbered 1 to 4 so as not to lose sight of their individuality during the tests.

Table IV gives the individual values and the averages of the tests.

(b). *Oxidation at 80° C.*—Each of the 2 sheets of each mixture gave on the one hand two rings, which were placed in two flasks (two rings from the same sheet in each flask) and were oxidized. On the other hand, two control samples (also two rings per sheet) were placed in identical flasks and subjected to a vacuum in a mercury vacuum pump at 0.01 millimeter pressure. The vacuum was maintained at this pressure for 48 hours in order to eliminate dissolved gases. The control flasks were then sealed and heated in the same way as the flasks containing the oxidized rings.

The test was stopped at an absorption of 0.9 per cent of oxygen, based on the rubber.

The mechanical tests were carried out after one day's rest, in the cold and in darkness. Table IV gives a summary of the experimental results.

(c). *Oxidation in the Cold in Diffused Light.*—The same kind of samples as in the preceding tests, but from two new sheets, were utilized in the same way. The experiment was stopped at the end of 13 months, the samples having absorbed 0.54 per cent of oxygen, based on the weight of the rubber. Table V summarizes the experimental results.

II. Mixtures with Tetramethylthiuram Disulfide

(a). *Preparation of the Mixtures.*—As with diphenylguanidine, two experiments were carried out, one on a laboratory mill and the other on a factory mill.

In the first test, milling was for 18 and 29 minutes. The viscosities were not measured.

In the second test, made on the factory mill, a mixture of 10 kilograms was used, and this was divided into three parts: one of 5 kilograms and two of 2.5 kilograms, corresponding to increasing times of work, but in this case carried out on the same mill.

These three test-pieces, marked TA, TB, and TC, were left to cool again after milling; then the two accelerators shown in Table II were added in the form of 10 per cent master batches. The samples were then immediately sheeted out to bring about more rapid cooling and to avoid scorching.

(b). *Viscosities.*—The viscosities were measured as usual with solutions of 1.66 gram of mixture per gram of raw rubber in 25 cubic centimeters of benzene.

The results were:

TA	31.1 seconds
TB	26.5 seconds
TC	16.8 seconds

The differences are relatively slight, a fact which confirms the statement made earlier that the mechanical effect is much less severe on large factory mills than on small laboratory mills.

(c). *Determination of the Optimum Time of Vulcanization as a Function of Mastication and of the Original Mechanical Properties.*—Mixture TA was vulcanized for 4, 7, 10, 13, and 16 minutes at 143° C., and the others only 7, 10, 13, and 16 minutes. Table VI gives the average results of these tests on 6 rings from each mixture. Figure 24 shows in another form, the slight difference between the optima of vulcanization for these three times of milling. The optimum time of vulcanization was around 7 minutes.

(d). *Oxidation at 80° C. (Fig. 26).*—From two sheets of each of the mixtures TA, TB, and TC, vulcanized for 10 minutes, six rings were oxidized at 80° C. and six control rings were placed in a vacuum under identical conditions, three rings being placed in each flask. The test was stopped at an absorption of oxygen of 0.67 per cent, based on the weight of the rubber.

The mechanical tests, carried out after the vulcanizates had stood in darkness for one day are shown in Table VI, which gives the average values. The control samples which had been placed in a vacuum underwent considerable alteration with respect to the original samples, doubtless as a result of overvulcanization. The oxidized rings were hardly any more deteriorated, and in any case mastication did not seem to hasten the deterioration particularly.

It should be noted, however, that these tests were carried out on samples which were slightly overvulcanized.

(e). *Oxidation in Diffused Light in the Cold* (Fig. 25).—The experiment, which lasted for 457 days or 15 months, was not continued long enough to give any appreciable change in mechanical properties. Nevertheless the proportion of oxygen absorbed, *viz.*, 0.26 per cent by weight of the rubber, was just sufficient to cause the first evidence of degradation.

For the mixture studied, a test of good resistance to oxido-aging is that it oxidizes only slowly, and in addition that it resists very well the oxygen absorbed.²⁴ Taking into consideration the fact that in our experiments the oxygen was under nearly normal pressure, or five times more concentrated than in the atmosphere, it is seen that under ordinary conditions of storage, such a mixture would be perfectly stable for a period of at least six years, and consequently would be stable very much longer from a practical point of view.

According to Table VII, the oxidized samples show better mechanical properties, at least in regard to their tensile strengths, than do the original samples. This fact, expressed by negative values of the percentage loss in relation to the original samples, confirms the fact that the latter were slightly undervulcanized. Storage at ordinary temperatures brought the rubber nearer to its point of optimum vulcanization before it showed the first indications of oxido-aging.

C. Influence of Heating Alone on the Oxido-Aging of Rubber

One-gram samples were placed in glass bulbs, which were connected with a mercury pump; the lower two-thirds of the bulbs were immersed in an oil bath, which could be heated at a temperature regulated exactly by an electric resistance. The vacuum was started at ordinary temperature until the mercury dropped to 0.01 millimeter, and this was maintained for 12 hours in order that the dissolved air might be removed from the bulb. The vacuum was again started at the end of this time, and the system was heated slowly to 80° C. This temperature was maintained for two hours. When at this moment one of the bulbs was cut off by means of a blow-pipe and the contents studied for its tendency to oxidize, it was found not only that this series of treatments had not altered the rubber but, on the contrary, that its tendency to oxidize had slightly diminished.

While the vacuum was maintained, the temperature of the bath was slowly increased to 143° C., which required one hour, and this temperature was maintained for two to four hours; finally the apparatus was allowed to cool, without interrupting the vacuum.

A considerable evolution of gas was observed during the first two hours of heating at 143° C., and furthermore there was a considerable deposit of volatile products in the upper unheated part of the bulbs. This deposit, which was a distillate of rubber, was composed of a mixture of white crystals in an oily magma, the relative proportions of which varied over a wide range depending upon the nature of the rubber, and for the same rubber, with the time of milling.

TABLE III
ORIGINAL MECHANICAL PROPERTIES OF SAMPLES DA AND DD FOR THE PURPOSE OF DETERMINING THE OPTIMUM TIME OF VULCANIZATION FOR EACH MIXTURE (SEE FIG. 23)

Time of Vulcanization (Minutes)		Tensile Strength (Av. Kg. per Sq. Mm.)	Percentage Elongation at Rupture (Average)
DA	40	1.50	580
	50	1.53	597
	60	1.54	598
	70	1.54	598
DD	40	1.41	597
	50	1.53	602
	60	1.53	588
	70	1.46	568

TABLE IV
EXPERIMENTS ON A MIXTURE, CONTAINING DIPHENYLGUANIDINE, OXIDIZED AT 80° C.
IN THE PRESENCE (SEE FIG. 20) AND IN THE ABSENCE OF OXYGEN

		Stored at 80° C.			Percentage Loss (Based on the Sample)	
		Original Sample	In Vacuum	In Oxygen (Absorption 0.9% of Wt. of Rubber)	Original	Stored in Vacuum
Tensile Strength (av. kg. per sq. mm.)	DA	1.56	1.56	0.85	45.5	45.5
		1.58	1.51	0.86	46	43
	DB	1.55	1.55	0.92	41	41
		1.51	1.64	1.05	30	36
	DC	1.67	1.76	1.06	36.5	39
		1.58	1.45	0.83	47	43
	DD	1.63	1.49	0.90	45	39.5
		1.63	1.60	1.00	38.5	37.5
Percentage Elongation at Rupture (average)	DA	567	556	465	18	16.5
		571	544	477	16	12.5
	DB	562	539	495	12	8
		555	559	492	11	12
	DC	573	559	507	12	9
		577	530	533	7	0
	DD	575	534	487	15	9
		573	552	492	14	11

TABLE V
EXPERIMENTS ON A MIXTURE, CONTAINING DIPHENYLGUANIDINE, STORED IN THE
COLD IN THE PRESENCE (SEE FIG. 19) AND IN THE ABSENCE OF OXYGEN

		Stored in the Cold			Percentage Loss (Based on the Sample)	
		Original Sample	In Vacuum	In Oxygen (Absorption 0.54% of Wt. of Rubber)	Original	Stored in Vacuum
Tensile Strength (av. kg. per sq. mm.)	DA	1.59	1.59	1.45	8.5	8.5
		1.54	1.82	1.45	6	20
	DB	1.66	1.75	1.23	26	29.5
		1.66	1.69	1.51	9	10.5
	DC	1.58	1.62	1.48	6	8.5
		1.58	1.77	1.58	0	10.5
	DD	1.59	1.62	1.59	0	2
		1.45	1.50	1.54	6	3
Percentage Elongation at Rupture (average)	DA	576	465	535	7	13
		560	545	499	11	9
	DB	570	540	431	24.5	20
		571	529	510	11	4
	DC	560	515	490	12.5	5
		563	473	510	9	7.5
	DD	579	510	523	9.5	2.5
		554	497	516	7	4

TABLE VI
EXPERIMENTS ON A MIXTURE, CONTAINING TETRAMETHYLTHIURAM DISULFIDE, STORED
AT 80° C. IN THE PRESENCE (SEE FIG. 26) AND IN THE ABSENCE OF OXYGEN

			Stored at 80° C.			Percentage Loss (Based on the Sample)	
		Vul- canized in Min.	Original Sample	In Vacuum	In Oxygen (Absorption 0.67% of Wt. of Rubber)	Original	Stored in Vacuum
Tensile Strength (av. kg. per sq. mm.)	TA	10	1.50	0.43	0.33	78	23
	TB	10	1.59	0.57	0.31	80	45
	TC	13	1.38	0.40	0.40	71	0
Percentage Elonga- tion at Rupture (average)	TA	10	508	249	178	65	28
	TB	10	518	277	174	66	36
	TC	13	505	251	241	52	4

TABLE VII
EXPERIMENTS ON A MIXTURE, CONTAINING TETRAMETHYLTHIURAM DISULFIDE, STORED
IN THE COLD IN THE PRESENCE (SEE FIG. 25) AND IN THE ABSENCE OF OXYGEN

	Sample	Time of Vulcani- zation (in min.)	Original Sample	Stored in the Cold		Percentage Loss (Based on the Sample)	
				In Vacuum	In Oxygen (Absorption 0.26% of Wt. of Rubber)	Original	Stored in Vacuum
Tensile Strength (av. kg. per sq. mm.)	TA	7	1.65	1.89	1.85	-12*	+ 2
	TB	7	1.65	1.82	1.85	-12*	- 1
	TC	10	1.38	1.67	1.29	+ 6	+23
Percentage Elonga- tion at Rupture (average)	TA	7	531	510	466	14	8
	TB	7	539	500	470	13	6
	TC	10	505	478	411	18	14

* The negative coefficients of loss of resistance indicate that the mechanical properties have been increased by storage at room temperature. This is due to an after-vulcanization which has brought the product, slightly undervulcanized at the beginning, to its point of optimum vulcanization before the deleterious effect of the oxygen has made itself felt to any considerable degree.

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- Since the viscosity coefficients of solutions were of interest only as a means of comparison, it was easier, as in earlier publications, to compare the rates of flow, i. e., values which, other things being equal, stand in inverse ratio to the viscosity coefficients. In this way the time required at a temperature of 20° C. for a four per cent solution of rubber in benzene to flow at the same temperature between the two marks of a viscometric pipette, the constants of which are given in the Experimental Section, is expressed in a uniform way.
- There are large variations from one experiment and another between the time of milling and the extent of mechanical work, evaluated by the viscosity. Surprising as it seems (we would refer to our earlier explanation¹⁶), the time of milling necessary to attain a given plasticization on a particular mill obviously depends upon the mass of rubber to be worked.
- The sudden rise (see Fig. 7) in the oxidizability of the two raw mixtures with tetramethylthiuram disulfide is due to vulcanization during the heating at 80° C.
- This supposition is in agreement with the fact, recently reported by van Rossem and Hessels,¹⁶ that heating at 80° C. diminishes the Russell effect, doubtless because of the destruction of the peroxides.
- The dimensions of this pipette have been given previously in the article mentioned.¹⁵ The pipette is a cylinder 13 mm. in internal diameter and 30 mm. long, drawn out at the lower part by a capillary 2.2 mm. in internal diameter and 150 mm. long. The upper part ends in a tube 5 mm. in diameter

on which is the first mark. The second mark is drawn on the capillary 58 mm. from the first. The volume between the two marks corresponds to a mass of water of 5.254 grams at 20° C.

²⁴ In connection with an investigation of litharge,¹⁴ we have shown that there are two types of defense against oxygen, one an antioxygenic effect and the other a diverting of the process of oxidation. The mixture studied here behaves very well from both points of view.

Discussion

P. BARY: In the present paper, two different methods have been used to measure the state of oxidizability of rubber, the direct measurement by the well-known method of Dufraisse, and that of determining the viscosity of solutions of milled rubber. Is there any relation between the two methods and do the comparative results follow the same law?

R. VIEILLEFOSSE: We have indeed utilized these two methods to determine the oxidizability, but for different products. The viscosity method enabled us to measure the degree of mastication, *i. e.*, the action of the oxygen absorbed during this operation. However, in order to determine the oxidizability after the different treatments (milling, vulcanization, etc.) the only method used was that first described by Dufraisse more than ten years ago. Accordingly we have not had an opportunity to compare the two methods referred to. However, as far as the oxidizability during milling is concerned, we have found curves with a hyperbolic trend mentioned by different investigators relating the viscosity to the time of milling, *i. e.*, in turn to the proportion of oxygen absorbed.

TH. BOUSSAND: Measurement of the viscosity is usually less reliable in following the changes in plasticity resulting from mechanical work; the results are hardly comparable, and the series of values found scarcely follows the actual changes in plasticity. This is the reason for instituting methods of measurement by compression or by extrusion through standard dies.

R. VIEILLEFOSSE: If the precaution is taken to submit the solutions, of which the viscosities are to be measured, to similar treatment and if substances of like composition only are compared, the values obtained are sufficiently exact for such studies as those we have had in view.

Among other causes of error is the phenomenon of thixotropy, which is common to numerous colloids and which involves changes in viscosity after any sort of mechanical agitation.

If the mistake is made of not having conditions, which from this point of view as well as from others, are strictly comparable, there is danger of obtaining inconsistent results.

This is why the viscosity measurement, which is very useful for a systematic laboratory study, cannot, as M. Boussand has very justifiably said, be of appreciable value in industrial operation.

M. BOUSSAND: All the phenomena of plasticization, vulcanization, and aging must be regarded from two points of view, chemical and physical, even if there are no relations between the concurrent variations of each of these phenomena.

Plasticization by mechanical work may involve a variable combination of oxygen, but it certainly involves also an extensive depolymerization, since even mixtures which have undergone the beginning of physical vulcanization and combination with sulfur can be plasticized. Mechanical work in which the rubber is sheeted off a mill continually has a very intense effect, in fact the action is around three times as rapid as by the ordinary method of milling with a rolling bank.

Vulcanization builds a new molecular structure, where many of the original differences are effaced. It is known in practice that severely masticated rubbers have a longer and greater plastic phase, that they vulcanize more slowly, and

combine with more sulfur to give products which are mechanically weaker than do less severely masticated rubbers. From the point of view of subsequent aging, the influence of vulcanization from a general point of view has scarcely been established, for example the enormous influence of the degree of vulcanization among other things. Moreover, technically correct vulcanization is rightfully chosen to correspond to the best aging; in general it is fifteen per cent less than that which gives the best mechanical properties. It seems to us that each mixture should be compared on the basis of the maximum resistance to aging.

It would certainly be of interest to know the comparative variations:

- (a) loss of mechanical properties,
- (b) time in the Geer oven,
- (c) proportion of oxygen combined with the rubber for the same losses (supposing that all the oxygen is combined with the rubber and not with the intermediate sulfurized products which may be derived from accelerators, proteins, etc.).

This would be for different degrees of vulcanization of the same mixture and for different types of mixtures. Perhaps it would be possible to discover, if not a law, at least interesting tendencies.

M. DUFRAISSE: I am in complete agreement with M. Boussand, who will perhaps allow me to add that, under a slightly different form, this is exactly the method we have used in our investigations on rubber.

We are now prepared to affirm that, except in very special cases, the results of mechanical tests, after treatment in the Geer oven, can be easily predicted by studying the proportion of oxygen absorbed. Whereas the first method is long, the second is rapid.

We have had occasion to study the question of oxidizability for certain factories, from which we have received samples. We have carried out measurements which were found to agree with aging tests made according to ordinary technic.

We are now developing a portable apparatus which is easy to manipulate, and which can be used readily in factories for the direct measurement of the oxygen absorbed. Among other advantages this method would make possible the examination of small quantities of a substance, for example one gram or even less.

L. GRAFFE: The fact, brought out by the experiments, that the disturbing factors which provoke the oxidation of rubber and its degradation disappear during vulcanization is very important to bear in mind. It may be explained by the fact that the oxygen absorbed during milling plays an active part in vulcanization and then disappears completely. It is known that during hot vulcanization hydrogen sulfide is always formed more or less abundantly, and it is capable of reacting with oxygen to form sulfur in a particularly active molecular state, thus: $\text{H}_2\text{S} + \text{O} \rightarrow \text{H}_2\text{O} + \text{S}$. What would seem to be proof of this is the fact that a small quantity of water is found in articles vulcanized in molds, *i. e.*, out of any contact with steam.

Thermal Plasticization of Rubber

I. Structural Changes in Thermally Plasticized Rubber

M. I. Farberov and Yu. Margolina

SCIENTIFIC RESEARCH INSTITUTE OF THE RUBBER INDUSTRY, MOSCOW, U. S. S. R.

It is well known that the plasticization of crude rubber by mechanical mastication is highly expensive, requires the use of large machines, and consumes great quantities of energy. The addition of softeners to facilitate and accelerate the mechanical treatment can be employed only within narrow limits, because an excess of softeners damages the quality of the finished goods.

A method of thermal treatment of rubber was recently proposed which gives the required degree of plasticization with a considerable reduction in the consumption of mechanical energy, and eliminates the use of softeners.

The process of thermal plasticization depends on heating sheeted or disintegrated rubber in a vacuum apparatus under exactly controlled conditions of temperature, vacuum, and duration of treatment.¹

According to the patent claims, the softened rubber has a number of advantages compared with rubber plasticized mechanically. It is distinguished by a high plasticity, at the same time involves no change in the vulcanization process, and does not impart inferior mechanical properties to the final product. It is claimed that the milling of rubber plasticized by thermal treatment is greatly facilitated, and the danger of scorching is considerably reduced. Cements of thermo-plasticized rubber have lower viscosities, making it possible to increase their rubber contents and to decrease the number of streaks in spreading.

A considerable number of published investigations on the changes in rubber during plasticization have disclosed that, depending on the degree of milling, the plasticity increases and the viscosity of its solutions decreases.

Based on the postulation of Hauser,² it was previously believed that in plasticization by roll milling a destruction of the hard integuments of the rubber globules and a mixing of their internal liquid contents with the solid external phase takes place. The resulting increased plasticity and decreased viscosity was explained by the liberation of the liquid rubber phase. In fact, the destruction of the hard integuments of the globules, composing the protein network of rubber, was observed under a microscope.³ However, the existence of a liquid internal phase in rubber globules was disproved by a subsequent investigation of Hauser, who proved that the contents of globules are liquid only in the latex and that it is converted into a solid gelatinous substance on drying or coagulation.

Thus the former explanation of the increase of plasticity and decrease of viscosity of rubber after milling on rolls proved to be inadequate. Many of the earlier investigators had suspected that atmospheric oxygen plays a considerable part in the milling of rubber, but, not being able to prove it, they concluded that this action of oxygen is not decisive. Further experiments, however, demonstrated beyond all doubt the highly important function of oxygen in plasticization. Thus Fisher and Gray⁴ discovered that rubber after milling on rolls for several hours in carbon dioxide became soft and slightly tacky, but showed only a slight change in its degree of unsaturation, whereas milling in air for several hours de-

creased it two per cent. They explained this phenomena by the oxidation or formation of cyclorubber. This was confirmed by Cotton⁵ by milling rubber in a closed mixer in air, nitrogen, and oxygen. The results of these tests led Cotton to the conclusion that rubber is completely unchanged in nitrogen, and that all changes during plasticization by milling in air, such as an increase in plasticity and weight and liberation of an aldehyde odor, are caused by the absorption of oxygen and the resulting oxidation.

These conclusions regarding the action of atmospheric oxygen on rubber during milling on rolls are supported by the investigations of Busse,⁶ who showed the formation of volatile peroxides. For an explanation of the formation of peroxides and the changes of rubber by milling, he advanced a theory of a chemical reaction between the rubber, activated by the mechanical action of milling, and oxygen, activated by the electric charge. In the thermal treatment of rubber, oxygen must also play a highly important part. Already van Rossem⁷ had noted that a depolymerization of the hydrocarbon takes place on heating rubber, which is accompanied by oxidation, and that the products of oxidation act as catalysts of the process of depolymerization.

By heating rubber in air, oxygen, a vacuum, hydrogen, and nitrogen, Fry and

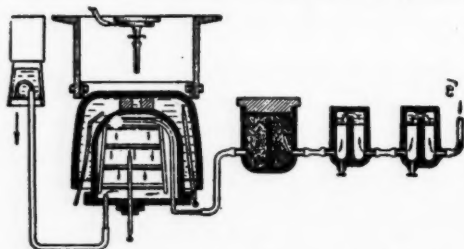


Figure 1—Scheme Used in Thermo-plasticization with Various Gases

Porritt⁸ demonstrated that the change in the viscosity of rubber solutions takes place only by milling in air or oxygen. By heating in a high vacuum, steam, hydrogen, and nitrogen at 150° C., the viscosity of solutions is unchanged. They concluded from this that the lowering of viscosity is caused by the interaction of rubber with oxygen. The same investigators showed that the changes of viscosity by heating

rubber are analogous to those obtained by milling. A very interesting study in this field was made by Grenquist,⁹ who heated rubber in air and water vapor at 150° C. and in oxygen and carbon dioxide at 70° C. Samples treated in this manner and those obtained by the usual milling for 5-90 minutes were tested for plasticity by the Williams method, and for destruction of the protein network by photomicrographs.³

The results of these experiments led Grenquist to conclude that the thermal disaggregation of rubber on heating is accompanied by oxidation, whereby oxygen is necessary to decompose the globular structure within the limits of the temperatures investigated.

On heating in water vapor, the globular structure remains, in his opinion, nearly unchanged, while the increase in plasticity is explained by thermal disaggregation, which is restored by rest. Hence the changed plasticity is more or less reversible if the globular structure is unimpaired.

Experimental Part

1. *Procedure.*—The object of the work was to ascertain the conditions of the technological process and to obtain a more or less complete picture of the changes which take place by the thermal treatment of rubber for different temperatures, times of treatment, and composition of the gaseous medium.

In distinction to other investigators, who merely determined either the viscosity of the rubber in solution or its plasticity, the purpose in the present work was to investigate the combined structural changes of rubber by these two methods. The rate of flow of rubber solutions under pressure was also measured in order to determine the character of their structural viscosity, and hence the extent of retention of the internal structure. To this end, the protein networks of the treated rubbers were photomicrographed.

As a start, five kilograms of smoked sheet were plasticized on a roll mill at 45–50° (16 × 30 in. diam., friction 1.33, clearance 4 mm.).

Alternate cuts on each side to about three-quarter of the length of the roll were made every minute. Samples were taken every 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, and 90 minutes. Another 5 kilograms of smoked sheet were milled on the same rolls

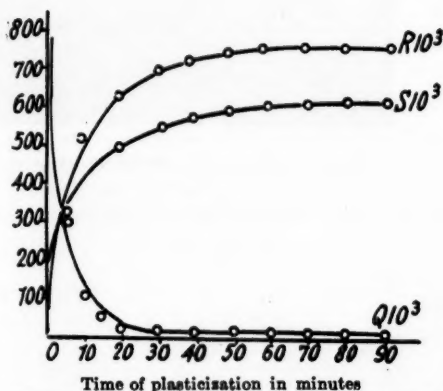


Figure 2—Plasticity of Rubber Plasticized on a Mill (Magnitudes R, S, and Q)

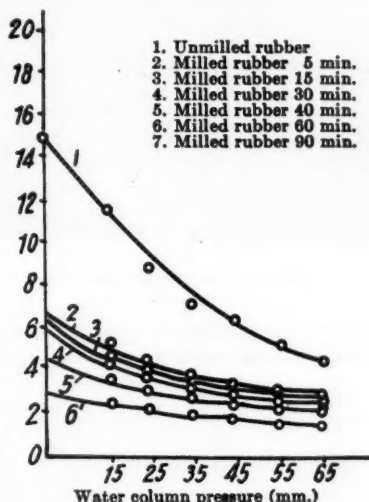


Figure 3—Structural Viscosity of Rubber Solutions Plasticized by Milling on Rolls

and the same temperature twice at a clearance of 2 mm. and thrice to obtain sheets 3 mm. thick which served as starting material for the experiments on thermal plasticization. These experiments were carried out in a laboratory autoclave with a thermometer and two holes in the lid. Vacuum was created by an oil pump, the residual pressure being 150, 75, and 35 mm. Oxygen, carbon dioxide, nitrogen, and ammonia, were conducted into the autoclave during the entire experiment at a definite rate by means of a tube reaching to the bottom of the autoclave and ending with a perforated spiral to assure a uniform current of gas (Fig. 1).

Three circular plates of rubber (total weight 15–16 grams), each resting on a separate shelf of the three-shelf wire support, were set into the autoclave heated in an oil bath fired by gas burners. Before starting each experiment the oil bath was heated 20–30° C. above the required temperature, the autoclave was then lowered into the oil bath, whereby the temperature of the autoclave was brought to a desired point within 15–20 minutes. After completion, the autoclave was rapidly cooled to room temperature by setting it into running water. After 24 hours of rest, the resulting samples of rubber were tested for plasticity, structural viscosity,

and degree of destruction of the protein network. The plasticity was tested in a Williams plastometer at 70° C. Samples weighing 1.84 grams of the exact volume of 2 cc. (d. 0.92) and height (H_1) from 8.3 to 8.5 cm. were held in a thermostat at 70° C. for 3 minutes; the calculations were made after 3 minutes (H_2); the recovery (H_3) of the original height of sample was determined also after 3 minutes.

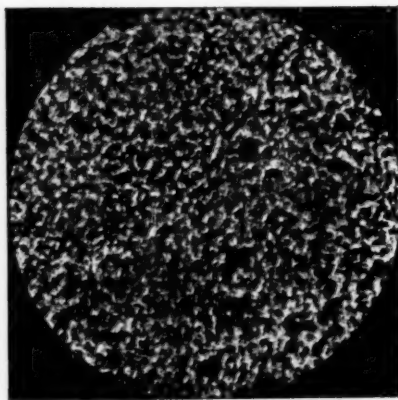


Figure 4—Unmilled Rubber

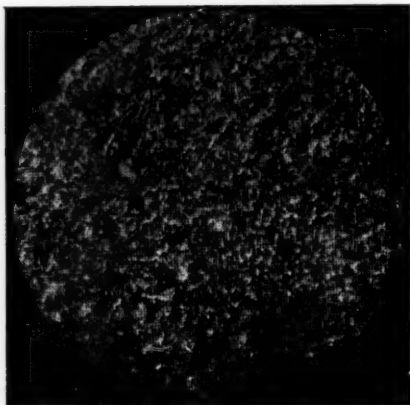


Figure 5—Rubber Milled for 40 Minutes

For characterizing the plasticity, besides the values H_2 and H_3 , the following magnitudes were determined:

$$S = \frac{H_1 - H_2}{H_1 + H_2},^{10}$$

which expresses the softness,

$$R = \frac{H_1 - H_2}{H_1}$$

residual deformation,

$$Q = \frac{H_3 - H_2}{H_1 - H_2}$$

and the relation between the elastic and complete deformation. This latter magnitude approaches zero with increase in softness, and approaches unity with increase in elasticity.⁹

The structural viscosity was determined in order to obtain a quantitative estimation of the changes in the internal structure of the rubber. This method is based on the known deviation of colloids from the Hagen-Poiseuille law. According to this law, the rate of flow of pure liquids through a capillary is, within certain limits, directly proportional to the pressure, and consequently their viscosities do not vary with change in pressure. Colloidal liquids, as was shown by de Waele, W. Ostwald,¹¹ and other investigators, do not obey this law, and their velocity of flow through a capillary is proportional to a certain n power of the pressure P . This deviation is quantitatively determined by the well known de Waele-Ostwald formula:

$$\eta = KP^{1-n},$$

where η is the relative viscosity, and the magnitude n is a measure of the deviation of a colloid from the Hagen-Poiseuille law and an index to the characteristics of its internal structure. Among the colloids investigated, rubber possesses the greatest value of the index of structural viscosity. For determining the structural viscosity and calculation of the magnitude n , the method of Dogadkin and Pevzner¹² was used. By this method it was found that the index of structural viscosity n diminishes with increase in the degree of milling, action of light, etc.

The rate of flow of a 0.75 per cent solution of rubber in benzene was measured at 25° C., and a water column pressure of 15–65 cm. in the Ostwald viscometer ($\mu = 0.447$).

Moreover the destruction of the globular structure of rubber was illustrated by photomicrographing the protein network. The photomicrographs were obtained by the method of Grenquist³ based on the relative lyophilic condition of the rubber proteins after treatment with boiling water. Crude rubber, optically void under ordinary conditions, becomes opaque after boiling in water and gives a microscopic picture of the protein integuments of its globules. Because of the lack of an apparatus for cutting thin slices, coarse cuts of rubber were pressed out at 60° C.

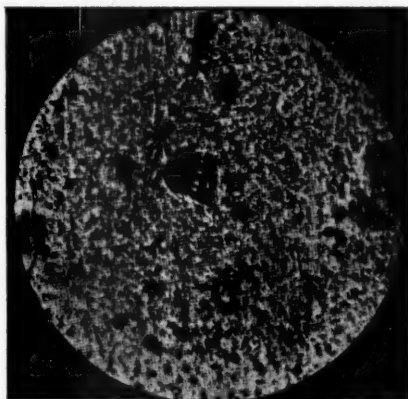


Figure 6—Rubber Milled for 90 Minutes

1. Original rubber
2. Thermally plasticized for 15 min.
3. Thermally plasticized for 30 min.
4. Thermally plasticized for 60 min.
5. Thermally plasticized for 90 min.
6. Thermally plasticized for 120 min.

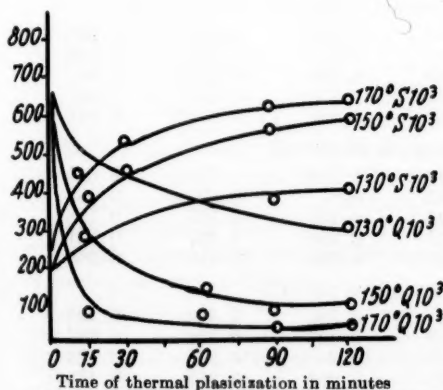


Figure 7—Plasticity of Rubber Thermally Plasticized at 170°, 150°, and 130° C. (Magnitudes S and Q)

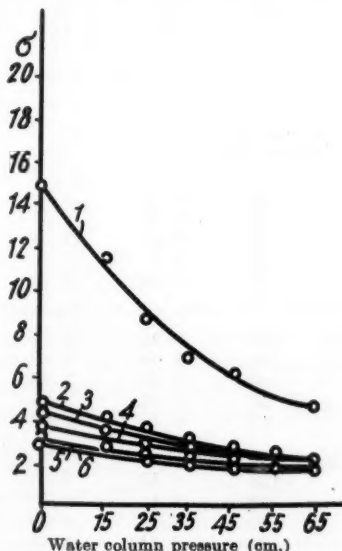


Figure 8—Structural Viscosity of Rubber Solutions Thermally Plasticized at 170° C.

and 5 kg. pressure. The thin slabs were kept in boiling water until opaque (2-4 min.) and laid on glass slides. A cover glass, wetted at the edges with water glass, was placed over it and the whole pressed as described above. After ten to fifteen minutes the cover glass was tightly and firmly attached to the slide, giving thin and

TABLE I
PLASTICIZATION ON ROLLS

Duration of Milling (Min.)	H_1	H_2	H_3	Plasticity S	R	Q
90	8.45	1.97	2	0.621	0.763	0.005
80	8.46	1.98	2.01	0.623	0.763	0.005
70	8.45	1.97	2	0.622	0.763	0.005
60	8.48	2.04	2.07	0.612	0.755	0.005
50	8.47	2.15	2.17	0.595	0.743	0.003
40	8.47	2.27	2.29	0.577	0.728	0.003
30	8.47	2.43	2.48	0.553	0.707	0.008
20	8.48	2.84	2.9	0.498	0.654	0.016
15	8.47	3.04	3.31	0.471	0.609	0.05
10	8.44	3.56	4.08	0.406	0.516	0.106
5	8.46	4.55	5.78	0.3	0.316	0.315
unmilled rubber	8.5	6.02	7.97	0.171	0.062	0.786

PLASTICIZATION ON A MILL
Viscosity

Water Column Pressure (in Cm.)	Unmilled Rubber	5	15	Time of Plasticization (Min.)				60	90
0	19.08	9.66	5.16	3.68	3.35	3.02	2.79		
15	14.7	8.5	3.61	2.56	2.43	2.3	2.17		
25	10.44	6.83	2.29	2.43	2.27	2.12	2.08		
35	8.87	5.77	3.15	2.35	2.26	2.02	2.01		
45	7.27	4.81	2.84	2.17	2.09	1.9	1.82		
55	6.38	4.35	2.69	2.09	2	1.84	1.7		
65	5.6	3.77	2.5	2.05	1.97	1.77	1.6		
η	1.65	1.53	1.25	1.14	1.13	1.12	1.1		

TABLE II
Plasticity

Duration of Heating (Min.)	H_1	H_2	H_3	S	R	Q
Thermal plasticization at 170° C.						
120	8.44	1.96	2.16	0.623	0.744	0.031
90	8.32	1.95	2.16	0.62	0.74	0.033
60	8.37	2.54	2.89	0.534	0.654	0.06
30	8.4	2.7	3.05	0.513	0.625	0.06
15	8.39	3.17	3.57	0.451	0.574	0.071
Thermal plasticization at 150° C.						
120	8.42	2.21	2.49	0.584	0.704	0.045
90	8.46	2.82	3.32	0.5	0.607	0.088
60	8.46	3.29	3.95	0.44	0.533	0.128
30	8.45	3.64	4.75	0.398	0.437	0.231
15	8.48	3.67	4.95	0.396	0.416	0.266
Thermal plasticization at 130° C.						
120	8.37	3.65	4.2	0.392	0.498	0.116
90	8.41	4.3	5.83	0.323	0.306	0.372
60	8.4	4.53	6.17	0.3	0.265	0.424
30	8.44	4.63	6.28	0.291	0.255	0.433
15	8.43	4.8	6.66	0.264	0.21	0.429
Original rubber	8.48	5.87	7.62	0.181	0.101	0.071

beautifully preserved preparations. They were photographed with a Zeiss apparatus at 440 magnifications.

2. *Plasticization by Milling on Rolls.*—Measurements of the plasticity showed a characteristic increase on milling for 20–30 minutes, after which the plasticity remained practically unchanged (Table I, Fig. 2). The reduction of the relative viscosity of rubber solutions in proportion to the degree of milling is shown in Fig. 3.

The magnitude of the index of the structural viscosity n , according to the de Waele-Ostwald formula, indicates a nearly complete destruction of the internal structure of the rubber after 20 minutes of milling.

The photomicrographs (Figs. 4, 5, and 6) give a characteristic picture of the undamaged globular structure of the unmilled rubber (Fig. 4) and its gradual destruction with progressive milling (Fig. 5, milling for 40 minutes), to a nearly complete disappearance of the protein network, and the formation of coarse aggregates from the residues of the protein integuments of globules (Fig. 6, milling for 90 minutes).

3. *Thermal plasticization* in air was carried out at 130°, 150°, and 170° C. for 15, 30, 60, 90, and 120 minutes. The thermal plasticization at 170° gave very tacky products (particularly after 120 minutes), with a sharply increased plasticity and decreased viscosity (see Tables II and VII).

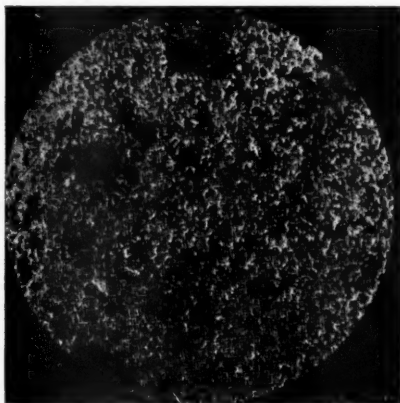


Figure 9—Rubber Treated in the Air at 170° for 120 Minutes

TABLE III

CHANGE IN THE INDEX OF STRUCTURAL VISCOSITY BY THERMAL PLASTICIZATION AT 130°, 150°, AND 170° C.

Duration of Heating (Min.)	Magnitude of n at		
	170°	150°	130°
Original rubber	1.59	1.59	1.59
15	1.44	1.54	1.59
30	1.41	1.54	1.57
60	1.4	1.49	1.56
90	1.34	1.46	1.55
120	1.3	1.39	1.48

Thermal plasticization at 150° C. gave less tacky products and less sharply defined changes in plasticity (Table II), structural viscosity (Fig. 10) and magnitude n (Table III). The thermal plasticization at 130° C. caused still smaller changes, as seen in Table II and Fig. 11. The comparatively small change in n (Table III) agrees with the smaller degree of destruction of the globular structure of rubber, as seen in Fig. 12.

4. *Thermal Plasticization in Vacuo.*—The experiments, carried out at 150° and 170° C. for 15, 30, 60, 90, and 120 minutes, demonstrate the great importance of the concentration of oxygen in the thermal treatment.

With decreasing air pressure and correspondingly decreasing oxygen concentration, the plasticization effect also decreased. Rubber treated at 35 mm. pressure was nearly untacky, whereas at 150 mm. pressure it retained considerable of its

tackiness. The plasticity change of rubber thermally plasticized *in vacuo* at 170° is shown in Fig. 13.

The structural viscosity of rubber solutions decreased in direct proportion to the residual pressure. The index of structural viscosity n changed in the following manner:

Duration of Heating (Min.)	Residual Pressure (Mm.)		
	35	75	150
15	$n = 1.55$	1.52	1.51
60	$n = 1.48$	1.45	1.43
120	$n = 1.38$	1.36	1.34

The thermal vacuum plasticization at 150° C. changed the plasticity and viscosity of rubber in an analogous manner, but to a correspondingly smaller degree.

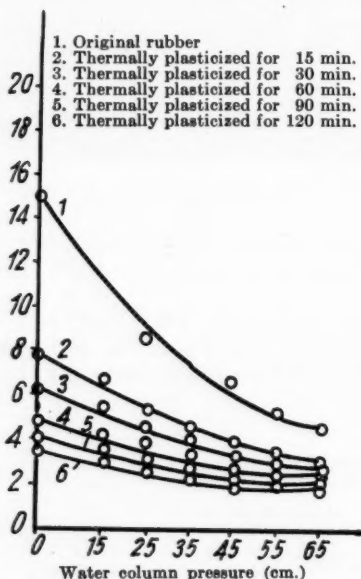


Figure 10—Structural Viscosity of Rubber Solutions Thermally Plasticized at 150° C.

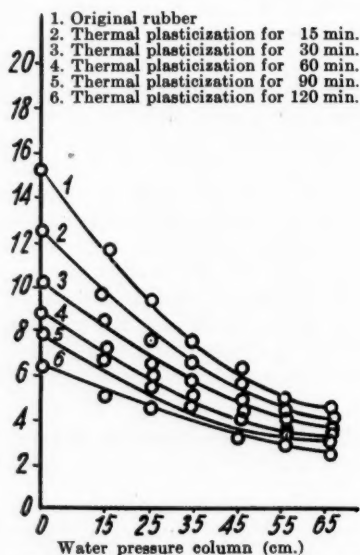


Figure 11—Structural Viscosity of Rubber Solutions Thermally Plasticized at 130° C.

The lowest value of the index n was 1.46 (at a residual pressure of 150 mm. and 2 hours of treatment).

5. *Thermal Plasticization in Oxygen.*—The thermal plasticization was carried out at 130°, 150°, and 170° C. for 30 minutes. Treatment at 170° gave a highly tacky, dark, almost liquid product with a sharply increased plasticity (Table IV), reduced viscosity (Fig. 14), and considerably destroyed globular structure (Fig. 15).

At 130° and 150° C. the changes were correspondingly smaller. The indices of structural viscosity n by treatment for 30 min. at 130°, 150°, and 170° C. were 1.47, 1.41, and 1.23, resp., *i. e.*, approximately equal to the values obtained by thermal plasticization for 120 minutes at equal temperatures. The effect of temperature on structural viscosity by thermal plasticization in oxygen is clearly illustrated by the curves in Fig. 14.

TABLE IV
THERMAL PLASTICIZATION IN OXYGEN AT 130°, 150°, AND 170° C. FOR 30 MINUTES

Heating for 30 Min. at	Plasticity					
	H_1	H_2	H_3	S	R	Q
170°	8.47	1.54	1.63	0.692	0.807	0.013
150°	8.49	2.73	2.88	0.513	0.66	0.026
130°	8.42	4.08	4.7	0.347	0.441	0.148
Original rubber	8.48	5.87	7.62	0.181	0.101	0.671

TABLE IVa
Plasticity

Thermal Plasticization in Carbon Dioxide at 170° C.

Duration of Heating (Min.)	H_1	H_2	H_3	S	R	Q
120	8.49	4.47	5.6	0.31	0.305	0.355
90	8.43	4.34	6.05	0.32	0.282	0.418
60	8.47	4.88	7.34	0.268	0.133	0.685
30	8.47	5.14	7.48	0.244	0.116	0.703

Thermal Plasticization in Nitrogen at 170° C.

120	8.36	3.69	4.59	0.387	0.451	0.196
60	8.47	3.83	5.93	0.377	0.299	0.445
30	8.45	4.78	6.37	0.277	0.246	0.433

Thermal Plasticization in Ammonia at 170° C.

120	8.48	4.22	5.79	0.335	0.317	0.368
60	8.46	5.13	6.36	0.245	0.189	0.519
30	8.5	5.36	7.49	0.226	0.118	0.678
Original rubber	8.48	5.87	7.62	0.181	0.101	0.671

6. *Thermal Plasticization in Inert Gases.*—Experiments at 170° C. for 60, 80, and 120 minutes showed little plasticization in the absence of oxygen. Before each experiment the air in the autoclave was expelled by conducting a strong current of gas for 30–40 minutes. Since the rubber was not freed from the adsorbed air, it must be accepted that traces of oxygen were invariably present in all cases.

TABLE V

Composition of Gaseous Medium Contents of O in kg. per liter	Air Pressure (Mm.)					Carbon dioxide	Nitrogen	Ammonia	Original Rubber
	Oxygen	760	150	75	35				
H_1	880.0	135	36.5	18.2	9.9
H_2	8.47	8.4	8.47	8.42	8.41	8.47	8.45	8.5	8.48
H_3	1.54	2.7	3.05	3.18	3.61	5.14	4.78	5.36	5.87
S	1.63	3.05	3.33	4.03	6.1	7.48	6.37	7.49	7.62
R	0.692	0.513	0.47	0.451	0.4	0.244	0.277	0.226	0.181
Q	0.807	0.626	0.548	0.521	0.393	0.116	0.246	0.118	0.101
Relative viscosity η	0.013	0.061	0.143	0.162	0.31	0.703	0.433	0.678	0.671
Index of structural viscosity n	2.87	4.35	5.6	5.99	6.32	14.74
	1.23	1.41	1.47	1.48	1.49	1.59

The results of experiments show (Table IVa) that thermal plasticization in carbon dioxide, nitrogen, and ammonia increased the plasticity of rubber only slightly, probably at the expense of the oxygen traces retained in the rubber. The globular structure of rubber remained almost undamaged (Fig. 16).

In the preparation of solutions of these samples of rubber, certain interesting phenomena were observed. Samples thermally plasticized in carbon dioxide, nitrogen, and ammonia could not be dissolved in benzene, even on standing for one month. Mechanical shaking somewhat increased their solubility, but failed to give

complete solutions. Heating also had no effect. The samples treated in ammonia showed the lowest solubility.

An explanation of the causes of this phenomenon and a study of the behavior of rubber in various gaseous media will require a special investigation.

A number of experiments on the direct determination of the oxygen absorbed by rubber by thermal plasticization in air were carried out in the following manner. First the contents of oxygen in the air contained in the autoclave was determined. Then, after thermal plasticization was completed, the autoclave was connected with a Brunte buret, and the oxygen was absorbed in an alkaline solution of pyrogallol. The difference between the original and the residual contents of oxygen in the air in the autoclave gave the oxygen absorbed by the rubber during thermal plasticization. Without considering the method entirely accurate, the results give some quantitative idea of the function of oxygen in the process; for example, the oxygen

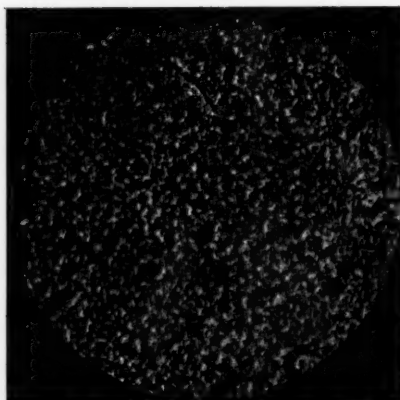


Figure 12—Rubber Treated in the Air at 130° for 120 Minutes

gallol. The difference between the original and the residual contents of oxygen in the air in the autoclave gave the oxygen absorbed by the rubber during thermal plasticization. Without considering the method entirely accurate, the results give some quantitative idea of the function of oxygen in the process; for example, the oxygen

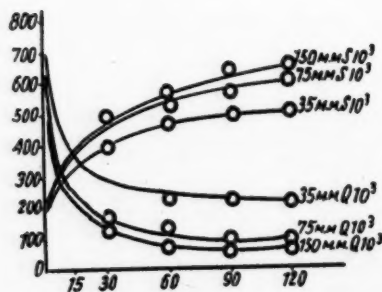


Figure 13—Time of Thermal Plasticization (Min.)

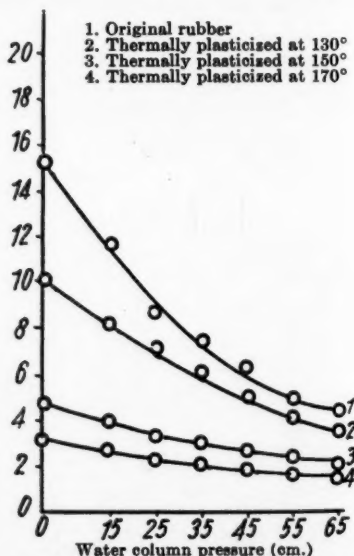


Figure 14—Structural Viscosity of Rubber Solutions Thermally Plasticized in Oxygen at 130°, 150°, and 170° C. for 30 Minutes

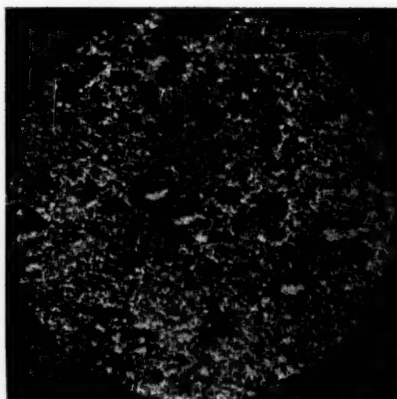


Figure 15—Rubber Treated in Oxygen at 170° for 130 Minutes

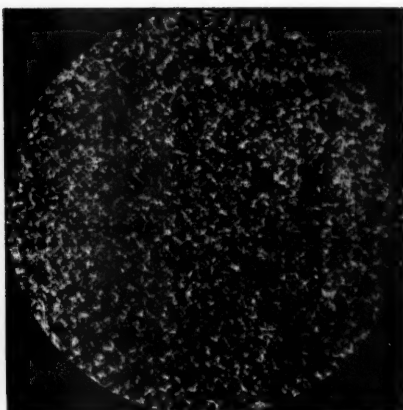


Figure 16—Rubber Treated in Carbon Dioxide at 170° C. for 120 Minutes

absorbed on thermal plasticization at 170° C. for 120 minutes was 0.517, for 60 minutes was 0.413, and for 15 minutes was 0.344 per cent.

Discussion

It is possible to conclude from the results that the changes of plasticity and internal structure of rubber during milling and thermal treatment run parallel; the plasticity increases and the recovery capacity, viscosity, and structural viscosity of solutions decreases in definite relations to the time of milling, and to the

1. Original rubber
2. Thermal plasticization with oxygen 9.9 mg. per liter
3. Thermal plasticization with oxygen 18.2 mg. per liter
4. Thermal plasticization with oxygen 36.5 mg. per liter
5. Thermal plasticization with oxygen 185 mg. per liter
6. Thermal plasticization with oxygen 880 mg. per liter

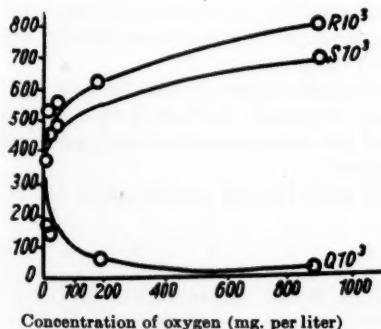


Figure 17—Plasticity of Rubber Thermally Plasticized at 170° C. at Different Concentrations of Oxygen in Mg. per Liter (Magnitudes R, S, and Q)

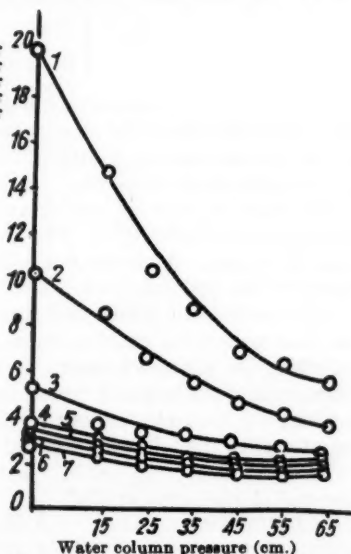


Figure 18—Structural Viscosity of Rubber Solutions Thermally Plasticized at 170° C. for 30 Minutes at Various Concentrations of Oxygen (Mg. per Liter)

temperature, time of heating, and the composition of the gaseous medium in the thermal treatment.

The determinant factor in the thermal plasticization of rubber is the concentration of oxygen, which is evident by a comparison of the plasticity and structural viscosity of samples treated at 170° C. for 30 minutes in oxygen, air, and *in vacuo*, and in carbon dioxide, nitrogen, and ammonia (Table V). The graphs (Figs. 17 and 18) also show that the plasticity invariably increases and the viscosity decreases with increasing content of oxygen in the gaseous medium. In an environment devoid of oxygen, plasticization proceeds very feebly, and it may be postulated that in the complete absence of oxygen (if the air adsorbed in rubber is removed) no plasticization at all will take place.

For a constant composition of the gaseous medium and at a constant temperature, the extent of the changes is governed by the time of thermal plasticization.

It is necessary to point out that temperature is a highly important factor. The data in Tables II and III and Figures 7, 8, and 11 show that a 2-hour thermal plasticization at 130° C. increased the plasticity and the viscosity to a smaller degree than did a 15-minute treatment at 170° C. The indices of structural viscosity n are 1.48 and 1.44, resp. At insufficiently high temperatures, thermal plasticization in air and oxygen gave nearly the same results. From Tables IV and II, it is evident that thermal plasticization at 170° C. for 30 minutes in oxygen gave a greater plasticity than that at the same temperature for 2 hours in air.

On heating at lower temperatures (130° and 150° C.) in oxygen, the changes were considerably smaller and approached the results in air. A comparison of the H_2 magnitudes and the relative viscosities supports this conclusion.

		170°	150°	130°
Relative viscosity η	In air	4.35	6.12	10.04
	In oxygen	2.87	4.48	9.43
H_2	In air	2.7	3.64	4.63
	In oxygen	1.54	2.73	4.08

It follows that the experiments of Grenquist on thermal plasticization in oxygen and carbon dioxide at 70° do not show the essential character of the process, because at this temperature no considerable changes of rubber can be expected, regardless of the nature and composition of the gaseous medium.

The reaction between rubber and oxygen proceeds with the greatest energy at temperatures of 150–70° C. The velocity of the reaction depends on the concentration of oxygen. At lower temperatures the reaction proceeds more slowly, and therefore this dependence is considerably less evident.

When comparing milled and thermally plasticized rubbers, it should be pointed out that samples of equal softness, S , differed essentially in their Q values, characterizing the relation between the elastic and the general deformation, and in the magnitude of the index of structural viscosity, n .

Thus, for example, milling for 90 minutes and thermal plasticization for 120 minutes gave the following results:

	H_1	H_2	H_3	S	R	Q	η	n
Thermal plasticization at 170° for 120 minutes	8.48	1.96	2.16	0.623	0.744	0.031	2.77	1.3
Milling for 90 minutes	8.45	1.96	2	0.621	0.763	0.005	2.78	1.1

A possible conclusion that thermal treatment causes less destruction of the internal structure of rubber than does milling requires confirmation experimentally.

Conclusions

1. The results of the experiments give a more or less complete picture of the relative changes in rubber brought about by mechanical and thermal plasticization, and show that there is an analogy between the two effects.

2. The fundamental factor in thermal plasticization is oxygen (for a given set of thermal conditions), whereby a definite numerical relation exists between the plasticization effect and the oxygen concentration. In the experiments described, the quantity of oxygen absorbed by rubber did not exceed 0.55 per cent at the maximum temperature and time of treatment (170° C. for 120 minutes). Thermal plasticization in a medium devoid of oxygen (in carbon dioxide, nitrogen, and ammonia) proceeds very feebly.

3. In treatment at reduced pressure (*in vacuo*), and consequently with a diminished oxygen content, the higher the vacuum, *i. e.*, the lower the concentration of oxygen, the less was the plasticization obtained.

4. The effect of temperature in thermal plasticization was evident in the acceleration of the reaction between rubber and oxygen. The most effective temperature was in the interval of 150° and 170° C.

5. For an equal plasticity, the internal structure of rubber was preserved to a greater degree after thermal treatment than after mechanical plasticization, judged by the structural viscosity, η , and the magnitude, Q .

6. It was observed that rubber treated at high temperature (170° C.) in carbon dioxide, nitrogen, and ammonia lost to a considerable degree its ability to dissolve in common rubber solvents.

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Thermal Plasticization of Rubber

II. Technical Characteristics of Softened Rubber

M. I. Farberov and A. V. Susliakov

INSTITUTE OF RUBBER INDUSTRY, MOSCOW

The first part of this work¹ established the fact that thermal plasticization produces in rubber the same changes as does mechanical mastication, *e. g.*, mastication on a mill.

However, the decisive factor in judging the practicability of the new method of plasticization is the comparative technological appraisal of both methods from the standpoints of power consumption, behavior in the uncured state, quality of the resulting vulcanizates, and diverse other technological requirements.

Hitherto the technological appraisal of thermally plasticized rubber—"softened" rubber—has not been systematically treated in the literature. The only references we have noted are the pamphlet of Typke and King, Ltd.,² and the note of G. E. Cholet.³

1. Production of Softened Rubber

The rubber we used for thermal plasticizing was crushed to uniform crumbs of 3-4 mm. size. The crushing was done as follows. Rubber in the form of separate sheets was loaded on 8 × 16 in. mills with tight rolls (nip of 0.5 to 1 mm.); the speed of the front roll was 15 revolutions per minute, while the back roll was stopped to intensify crushing. The bulk volume of one kg. of rubber crumbs thus obtained amounted to six liters. The crumbs were put on trays in a uniform layer about 50 mm. thick.

Thermal treatment was effected in a laboratory vulcanizer 900 × 600 mm., with a steam jacket and a thermo-regulator. The steam pressure available did not permit a temperature above 150°, so all the experiments on thermal treatment were conducted at this temperature.

The experiments described in the first part of our work¹ proved conclusively that the basic factors in thermal plasticization are the concentration of oxygen in the medium, and the temperature. The vacuum treatment recommended by British patent No. 368,902⁴ is not absolutely necessary, for, as we have proved, the increase of vacuum, and consequently the decrease of oxygen concentration, reduces the plasticizing effect. 150° and 170° C. have proved to be the most effective temperatures.

Preliminary experiments showed likewise that the concentration of oxygen per 1 kg. of product is of some importance. Our purpose being to obtain 2 kg. of "softened" rubber in one batch, we increased the oxygen concentration by raising the air pressure inside the vulcanizer to 1.5 atm. (air-gage).

After thermal treatment, the rubber was cooled under room conditions to 50° C. and passed three times through heated mills (65° to 70° C.).

These strictly standard conditions were maintained in all thermal treatments.

2. Dynamics of the Plasticizing Process

The dynamics of the plasticizing process by both methods are of great interest in relation to the time factor. The curves of Fig. 1 for mechanical mastication, and of Fig. 2 for thermal plasticization are a graphic proof of this.

Mechanical mastication was conducted under strictly standard conditions shown on the figure. Plasticity was determined at 70° C. by the Williams method. The initial height of a rubber column of 2 cc. volume (H_1) was maintained within the range 8.3–8.5 mm. Its height (H_2) after three minutes pressure under the weight of the plastometer showed the "softness" of the sample, while the height (H_3) three minutes after the load was removed expressed "recovery," proportional to the elastic deformation of the sample.

An examination of the curves in Fig. 1 confirms the comparatively long known fact, that mechanical plasticization is especially effective at the beginning of the process, but becomes slower with the progress of mastication. Plasticity and re-

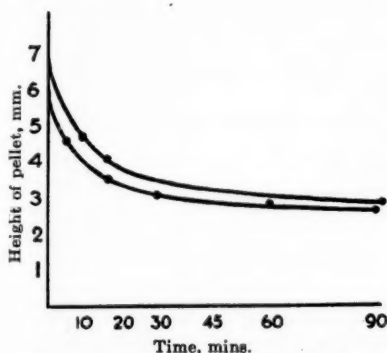


Figure 1—Plasticity of Smoked Sheet. (Masticated on 16" × 32" Mill at 50° C., Friction 1.33.) Upper Curve: Recovery (H_3). Lower Curve: Compression (H_2)

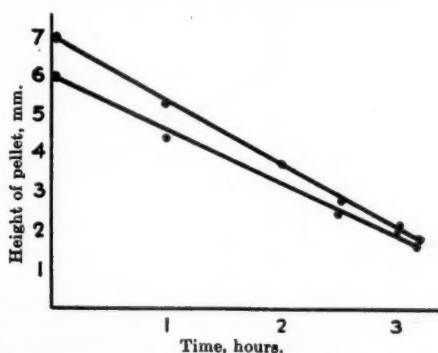


Figure 2—Plasticity of Smoked Sheet. (Thermally Plasticized, 2 kg. Heated at 150° C. Under 1.5 Atm. Air Pressure.) Upper Curve: Recovery (H_3). Lower Curve: Compression (H_2)

covery curves are, according to Williams, curves of approximately the second order. It is interesting to note that in the conditions of thermal plasticizing above described the effect is linear; the plasticity changed in direct proportion to the increase of time of thermal treatment (Fig. 2).*

3. Power Consumption with Varieties of Softened Rubber

In judging the advantages of this or that process of plasticization, the basic question is the power consumption in the preparation of stock.

In this connection we made a number of experiments on laboratory mills 16 × 32 in. Power consumption was registered by a Hartmann and Braun automatic wattmeter. We are able to describe only a few of these experiments here.

The curve in Fig. 3 shows the relation between power consumption and the resulting plasticity of the rubber.

For this experiment five kg. of rubber were worked on 16 × 32 in. mills for 90 minutes at a temperature of about 50° C. under strictly standard conditions. A sample of about 30 grams was removed 5, 10, 20, 30, 45, 60, and 90 minutes after the beginning of the process, to determine plasticity. The curve shows a *very sharp increase in power consumption for the purpose of obtaining products of appreciably*

greater degrees of plasticity. If 1.675 kilowatt-hours are required to obtain the product with $H_2 = 4.6$, it takes 3.25 kilowatt-hours to obtain the product with $H_2 = 3.6$, and 13.75 kilowatt-hours to obtain the product with $H_2 = 2.6$. According to our curve it is very difficult, and it takes a great deal of power, to obtain products of greater plasticity by means of *continuous* mastication on mills.

We made a further comparison of the power consumption for the production of three typical stocks: (1) a "pure" stock, without any fillers; (2) a tread stock; and (3) a heavily loaded stocks for brown soles. The formulas for the two first stocks are given below; the formula for the soling stock contained 32 per cent of rubber and 62 per cent of fillers (magnesium carbonate and kaolin 50:50).

The following three varieties of softened rubber from smoked sheet were used in the preparation of these stocks:

- (a) Rubber worked on a mill for 20 minutes, with plasticity $H_2 = 3.50$.
- (b) Mixed rubber consisting of 50% of *unsoftened standard smoked sheet rubber*, and 50% of *thermally plasticized rubber*, with $H_2 = 2.60$.

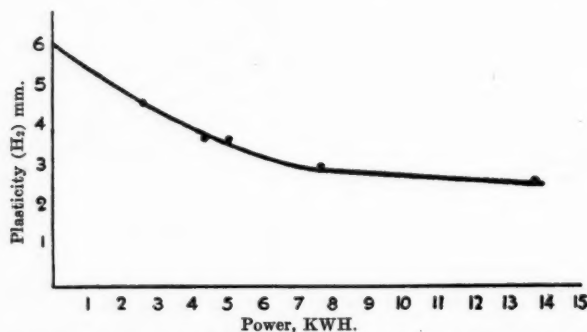


Figure 3—Variation of Plasticity with Power Consumption. (5 Kg. Smoked Sheet on 16" × 32" Mill)

- (c) Thermoplasticized rubber, with $H_2 = 2.60$.

Table I shows the plasticities of these types of rubber and of the stocks made from them.

TABLE I
PLASTICITY OF RUBBER AND OF STOCKS MADE FROM THEM

Type of Rubber	Rubber		Pure Gum Stock		Tread Stock		Soling Stock	
	H_2	H_1	H_2	H_1	H_2	H_1	H_2	H_1
(a) Rubber worked on the mills for 20 min.	3.50	3.80	2.23	2.36	3.41	3.65	7.14	7.41
(b) 50% of unsoftened rubber, plus 50% of thermally plasticized rubber	6.02	7.12	2.44	2.55	3.19	3.31
(c) Thermoplasticized rubber	2.60	2.78	1.91	2.04	2.61	2.70	6.63	6.78

Table II gives the *time of preparation* for these three stocks with different types of rubber.

Table III shows *power consumption* in watt-hours required to obtain 5 liters of each of the three stocks prepared with a different type of rubber.

Further, Table III shows also the power consumption for *individual operations*. Mechanical plasticizing on mills for the standard (a), crushing for the preparation

TABLE II
TIME FOR COMPLETING THE MIXINGS IN MINUTES

Type of Rubber	(a)			(b)			(c)		
	20 Min. Milling			50% Unsoftened + 50% Thermoplastic			Thermoplastic		
	Warm-ing of Rubber	Mixing	Total	Warm-ing of Rubber	Mixing	Total	Warm-ing of Rubber	Mixing	Total
Stocks									
1. Pure stock	2.0	14.0	16.0	2.0	14.0	16.0	1.0	12.5	13.5
2. Tread stock	1.5	23.5	25.0	1.5	23.0	24.5	1.0	17.0	18.0
3. Soling stock	1.0	34.0	35.0	1.0	28.5	29.5

of crumbs for thermoplastic rubber (b), and the process of preparation of the stock proper.

TABLE III
POWER CONSUMPTION IN WATT-HOURS FOR FIVE LITERS OF STOCK

Type of Rubber	(a)			(b)			(c)		
	Plasti-cization	Mix-ing	Total	Crush-ing	Mix-ing	Total	Crush-ing	Mix-ing	Total
Stocks									
1. Pure gum stock	2944	2655	5599	504	2857	3361	1008	1740	2748
2. Tread stock	2576	3757	6333	441	4005	4446	882	2360	3242
3. Soling stock	1840	5910	7750	630	5070	6700

Plasticizing of 5 kg. of smoked sheet, 20 min., to $H_2 = 3.50$, required 3860 watt-hours.

Crushing of 1 kg. of smoked sheet required 252 watt-hours.

Table III shows that when the mixture of unsoftened rubber with thermoplasticized rubber (b) was used, a saving of power of 40 per cent was effected for the pure gum stock, and of 30 per cent for the tread stock, compared with the standard masticated rubber (a).

When thermoplastic rubber alone was used, the saving of power was increased to 51 per cent for pure stock, 41 per cent for tread stock, and 14 per cent for soling stock. This is in agreement with the natural expectation that *the more rubber there is in the stock, the greater is the effect of using thermoplasticized rubber.*

The more considerable saving of power with thermoplasticized rubber alone is, of course, due to the greater plasticity of the product, which facilitates the introduction of ingredients and reduces the total time required for the preparation of the stock.

We made special experiments, using standard masticated and thermoplasticized rubbers of the same degree of plasticity ($H_2 = 3.6$), and found that essentially the saving of power was due to the elimination of the process of mechanical mastication, and amounted to 25-30 per cent. *The greater was the plasticity of rubber required for the preparation of the stock in question, the greater was the saving of power by changing from the standard masticated rubber to thermoplasticized rubber.*

Particular attention should be called to the stocks made with 50 per cent of unsoftened standard rubber, plus 50 per cent of thermoplasticized rubber with $H_2 = 2.6$. Tables I and II show that the time taken to prepare these stocks and their plasticities, did not differ from those of the stocks prepared with rubber worked on the mills (rubber "a"), whereas the saving in power was considerable (see Table III).

4. Mechanical Properties of Vulcanizates

In technological comparisons of both methods of plasticization, a most important question is that of the quality of the vulcanizates. We made a series of tests in order to elucidate this question (See Table IV).

We took for these experiments rubber plasticized by both methods approximately to an equal degree of plasticity. The mechanically masticated rubber had $H_2 = 3.44$; $H_3 = 3.76$, while the thermally plasticized rubber had $H_2 = 3.30$, $H_3 = 3.80$.

Two typical stocks, "pure gum" and tread, were prepared from these rubbers, as follows:

Pure Gum Stock		Tread Stock	
Rubber	100.0	Rubber	100.0
Zinc oxide	7.5	Zinc oxide	10.0
Pine tar	1.0	Gas black	40.0
Stearic acid	1.0	Pine tar	3.0
Ruberax	3.0	Stearic acid	3.0
Phenyl- β -naphthylamine	1.0	Phenyl- β -naphthylamine	1.0
Mercaptobenzothiazole	0.5	Mercaptobenzothiazole	0.6
Sulfur	3.0	Sulfur	3.0

These stocks were vulcanized over ranges of time. The samples were then subjected to normal mechanical tests in strictly identical conditions, both before and after aging (tensile tests were made on dumb-bell samples on a Scott machine). In Table IV we give only a small part of the numerical data for two different curing times.

TABLE IV
COMPARATIVE MECHANICAL PROPERTIES OF VULCANIZATES MADE WITH ORDINARY MASTICATED AND THERMOPLASTICIZED RUBBERS (OF EQUAL DEGREE OF PLASTICITY)

Curing Time in Min. at 138°	Modulus in Kg./Cm. ²		Tensile Strength in Kg./Cm. ² (P)	Elong. at Break in % (e)	Tensile Product (P. l) (100)	Resistance to Tear in Kg./Cm.
	300% (Elong.)	500% (Elong.)				
1. <i>Pure gum stock</i>						
(a) Standard masticated rubber (H ₂ = 3.44; H ₃ = 3.76)						
30	8.5	25	207	820	1700	47
45	10.0	28	206	816	1688	54
(b) Thermoplasticized rubber (H ₂ = 3.30; H ₃ = 3.80)						
30	10.5	25	210	812	1705	52
45	11.5	30	198	808	1595	55
2. <i>Tread stock</i>						
(a) Standard masticated rubber (H ₂ = 3.44; H ₃ = 3.76)						
30	57	165	263	664	1746	141
45	64	171	269	636	1712	178
(b) Thermoplasticized rubber (H ₂ = 3.44; H ₃ = 3.80)						
30	56	145	247	671	1653	153
45	67	180	270	633	1708	178

NOTE

1. The tearing test was carried out by the Winkelman-Goodrich method, the samples being of crescent shape.

2. The aging coefficient expresses in per cent the ratio between the tensile product of the stock after aging to the tensile product before aging. Aging by Geer method was done in an oven at 70° C. Aging by Bierer-Davis method was done in a bomb at 70° under oxygen pressure of 20 atm.

3. Abrasion tests were done on Williams-Goodrich machine, the results being the loss in cc. per H. P.-hour.

3	Coefficient of Aging Aging by Geer Method in Days			Coefficient of Aging Aging by Bierer-Davis Method in Hours		Resistance to Abrasion in Cc./H.P.-Hour
	7	10	14	48	96	
1.04	0.94	0.92	0.92	0.91	0.88	...
1.08	0.81	0.69	0.63	0.92	0.81	...
1.05	0.93	0.88	0.66	0.88	0.80	...
1.02	0.85	0.73	0.54	0.81	0.72	...
1.03	0.93	0.88	0.91	0.80	0.80	200
0.92	0.85	0.89	0.79	0.84	0.76	190
1.05	1.01	0.94	0.94	0.90	0.80	220
0.92	0.90	0.90	0.77	0.90	0.76	216

The data of Table IV show that the quality of vulcanizates obtained from mechanically or thermally plasticized rubbers having equal degrees of plasticity do not differ from one another in any way (within the range of experimental error) either before or after aging.

TABLE V
COMPARATIVE MECHANICAL TESTS ON VULCANIZATES MADE WITH STANDARD MASTICATED RUBBER AND WITH THERMOPLASTICIZED RUBBER WITH DIFFERENT DEGREES OF PLASTICITY

Curing Time in Min. at 138° C.	Modulus at 500%	Tensile Strength (P)	Elongation at Break (e)	Tensile Product	Coefficient of Aging 3 Days	Coefficient of Aging 7 Days
1. Standard masticated rubber ($H_2 = 3.50$; $H_3 = 3.80$)						
(a) Pure gum stock with 3% sulfur						
45	36	190	745	1423	1.02	1.00
(b) Pure gum stock with 3.5% sulfur						
45	38	195	743	1445
2. Thermoplasticized rubber ($H_2 = 2.6$; $H_3 = 2.78$)						
(a) Pure gum stock with 3% sulfur						
45	37	166	748	1242
(b) Pure gum stock with 3.5% sulfur						
45	38.5	186	760	1411	1.2	1.06

But if results are compared for rubbers of unequal plasticities, for example, if standard masticated rubber (a) is taken with a plasticity of $H_2 = 3.50$; $H_3 = 3.80$, and thermoplasticized rubber (b), with a plasticity of $H_2 = 2.6$; $H_3 = 2.78$, then, of course, the quality of the vulcanizates produced from the latter is inferior (Table V). We found, however, that by increasing the sulfur by 0.5 (per 100 parts of rubber) the quality of the vulcanizates (using thermoplasticized rubber) was raised to the quality of the vulcanizates made with standard masticated rubber. (In Table V results are given only for the pure stock.)

Stocks (both pure and tread) made from the mixture of 50 per cent of unsoftened rubber and 50 per cent of thermoplasticized rubber (see rubber "b" of Table II) do not differ in any way in mechanical properties either before or after aging, from the stock made with standard masticated rubber (rubber "a" of Table II). We cannot, however, give the respective data here.

5. Some Other Peculiarities of Thermally Plasticized Rubber

Calender Effect.—A comparison of calender effect in both varieties of softened rubber is of some interest. The determination of the calender effect was done as follows, according to the De Visser⁵ method.

Carefully selected smoked sheet was divided into two parts. One part was treated thermally until its plasticity reached $H_2 = 2.50$, $H_3 = 2.80$, while the second

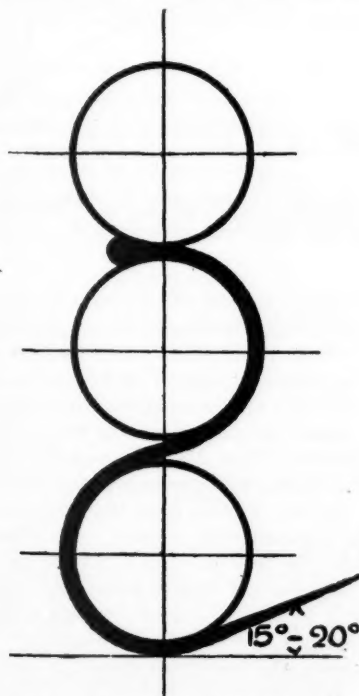


Figure 4—Scheme of Calendering

part was worked on a mill at 50° until approximately the same plasticity, $H_2 = 2.5$; $H_3 = 2.75$, was attained (the milling was done carefully to avoid any air blisters).

Before calendering, both softened rubbers were placed for two hours in an oven at 80° C. (the temperature of calendering). Calendering was done under the conditions shown in Fig. 4. The smooth sheet of rubber, $1\frac{1}{2}$ mm. thick drawn out from the calender, was put on a zinc-lined table, covered with a layer of soapstone (to allow free setting). The following day samples of dumb-bell type were tested on a dynamometer (30 kg. capacity).

From each sheet six samples were cut lengthwise, and six crosswise. The experiment was repeated four times, and the results were identical. The data in Figs. 5A and 5B represent the averages of four series of parallel tests.

The figures give the results of testing strips of calendered sheets, cut lengthwise and crosswise of the calender (*a*) for standard masticated rubber, and (*b*) for thermoplasticized rubber. As may be seen from the curves, the calender effect for the latter is considerably lower than for ordinary masticated rubber (the angle charac-

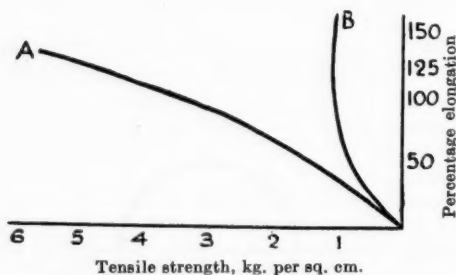


Figure 5A—Strength of Calendered Sheet. (From Masticated Rubber, $H_2 = 2.50$, $H_3 = 2.75$. A, Lengthwise; B, Crosswise)

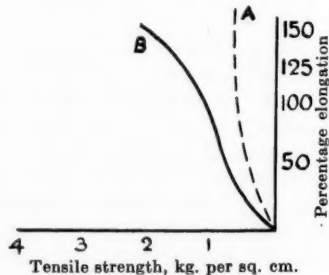


Figure 5B—Strength of Calendered Sheet. (From Thermally Plasticized Rubber, $H_2 = 2.25$, $H_3 = 2.80$. A, Lengthwise; B, Crosswise)

terizing calender effect is equal to about 50° for the ordinary masticated rubber, and 20° for the thermoplasticized rubber).

Water Absorption.—As is well known, water absorption is closely connected with the characteristics of rubber as in electric insulating material; the less water absorbed by rubber or stock, the better is its insulating quality.

From calendered rubber sheet (the plasticity in both cases was approximately the same $H_2 = 2.80$; $H_3 = 3.10$), 1.75 mm. thick, were cut samples approximately 2×2 cm., which were kept for 1–11 days in distilled water at 25° C.

As may be seen from the curves of Fig. 6, thermoplasticized rubber is characterized by a considerably smaller water absorption capacity. This is evidently connected with the destruction of a part of the hydrophilic proteins by thermal treatment.

Viscosity of Rubber Solutions.—Solutions of 3, 5, 7.5, and 10 per cent concentration were made under identical conditions from rubber treated by both softening methods, and of different plasticity. The viscosities were determined by Stormer's viscometer (results expressed in seconds per 100 revolutions of the cylinder).

It is clear from the curves of Fig. 7, that thermoplasticized rubber with an average degree of plasticity of $H_2 = 2.5$ and $H_3 = 2.75$ gives somewhat less viscous solutions than ordinary masticated rubber. For heavily masticated products ($H_2 = 1.85$) thermoplasticized rubber yields more viscous solutions.

6. The Use of Thermoplasticized Rubber in Production Mixings

We carried on extensive experiments on the application of thermoplasticized rubber for different industrial stocks. Of particular interest is, of course, the application of the material for those stocks which require very plastic rubber, as in this case there would be a particularly great saving of power. Foremost among these

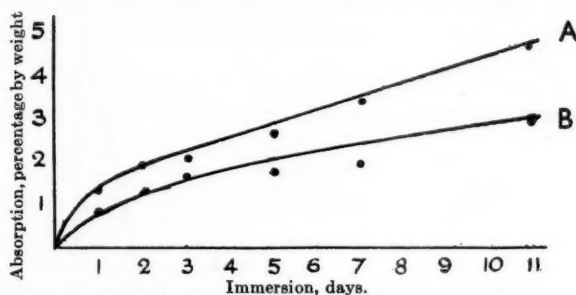


Figure 6—Water Absorption 25° C. (A Standard Masticated Rubber; B. Thermally Plasticated Rubber)

stocks are friction stocks for fabrics, sponge stocks, stocks for proofed fabrics, etc. We are compelled here to content ourselves with a short description of certain peculiarities of these stocks.

Friction Stocks.—In addition to the usual mechanical tests, we have carried out adhesion tests on an experimental five-ply belting frictioned with stock of the same composition made with standard masticated and thermoplasticized rubbers. The belt was tested by the usual separation method on a Schopper dynamometer and by a flexing method on a Scott flexing machine.

As is seen from Table VI, not only is thermoplasticized rubber satisfactory, but is even superior to standard masticated rubber in strength of adhesion of belting plies.

	Separation Method ¹ (Schopper Dynamometer)			Flexing Method ² (Scott Flexing Machine)	
	Maximum	Minimum	Average	Maximum	Minimum
Standard masticated rubber ($H_2 = 3.5$)	12.7	6.2	9.5	18700	23800
Thermoplasticized rubber ($H_2 = 3.5$)	16.1	8.7	12.4	25500	34000

¹ The results are given in kg. per 25 mm. of width of belting.

² Diameter of pulley, $1\frac{1}{4}$ in.; tension, 100 lb.; results are given in cycles (the machine making 170 cycles per minute).

Sponge.—Stocks used for the manufacture of sponge rubber represent a particularly attractive object for the use of thermoplasticized rubber. It is well known that these stocks call for a high degree of plasticity ($H_2 = 1.0$ – 1.8). This, of course, involves a considerable consumption of power and a long treatment on a mill. In our experiments, when mastication was done in four periods with intervals, 1.89 kilowatt-hours were required to produce 1 kg. of softened rubber for sponge ($H_2 = 1.5$).

The quality of sponge made from thermoplasticized rubber is excellent, and not inferior to the quality of sponge made from standard masticated rubber. Both artificial and natural aging is good.

Proofed Fabrics.—Stocks for proofed fabrics are also an interesting object for the use of thermoplasticized rubber. The ease of getting more plastic products makes it possible to work with more concentrated solutions (1:1). When proofing fabrics by calendering, high plasticity in the stock produces a very fine coating.

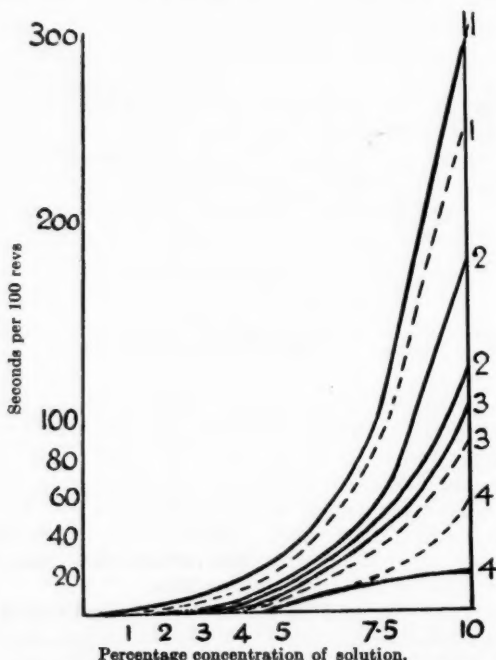


Figure 7—Solution Viscosity (Stormer's Viscometer, Full Lines, Standard Masticated Rubber, Dotted Lines, Thermally Plasticized Rubber)

Curve	Type.	Plasticities of Rubbers Used in Solutions.				Softness, H ₂				Recovery, H ₂			
		1	2	3	4	1	2	3	4				
Standard		2.79	2.47	2.13	1.86	2.95	2.58	2.29	1.87				
Masticated													
Thermally													
Plasticized		2.74	2.40	2.03	1.86	3.05	2.65	2.26	2.10				

In all cases the quality of the product is good.

Water Dispersion.—It is interesting to note that water dispersion of thermoplasticized rubber is more difficult than that of standard masticated rubber. It requires a somewhat greater concentration of the dispersing agent (alkali).

Conclusions

1. The method of thermal plasticization makes it possible to prepare rubbers of widely varying but regulated degrees of plasticity.

2. The use of thermally plasticized rubber gives a considerable saving of power in the production of stock. In our experiments the saving of power amounted to 15-50 per cent, depending upon the proportion of rubber in the stock and on the required plasticity. The greater the proportion of rubber, and the more plastic

the rubber required for the stock in question, the greater will be the saving in changing from ordinary masticated rubber to thermoplasticized rubber.

Based on equal plasticities, the saving is due essentially to the elimination of the process of mechanical mastication.

3. Mechanical properties of vulcanizates made from thermoplasticized rubber, both before and after aging, are in no way inferior to those of vulcanizates made from ordinary masticated rubber, if the plasticities of the rubbers are equal.

4. Thermoplasticized rubber has a smaller calender-grain effect than standard masticated rubber.

5. Thermoplasticized rubber is distinguished by a considerably smaller water absorbing capacity (about one-half) than ordinary masticated rubber.

Literature

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² "Softened Rubber," Pamphlet of Typke and King, Ltd. 1933.

³ P. E. Cholet, *Ind. Rubber World*, 1/3/1935.

⁴ British Patent No. 368,902 (Ungar and Schidrowitz) (1932).

⁵ De Visser, "The Calender Effect and the Shrinking Effect of Unvulcanized Rubber." London. 1926.

* Similar results for mechanical and thermal plasticizing processes (particularly at the temperature of 170° C.) were shown in the first part of our work.¹ In both cases the plasticizing effect was especially significant at the beginning of the process, becoming slower as the change proceeded.

As regards thermal plasticizing, however, this is true only of laboratory tests. Due to the small quantity of material in the laboratory, the heating and oxidation conditions are uniform for any part of rubber. But under the conditions described here, on a semi-industrial scale, the unequal effect of heat and oxygen upon the entire mass of rubber prolongs the first and most effective stage of the plasticization, the result being that the curve does not show the characteristic bend, and approximates instead a straight line.

Thermal Plasticization of Rubber

N. Gusev, Gruzevich, Khovrina, and Tzelikov

CENTRAL LABORATORY OF THE YAROSLAVSKIĬ WORKS

Preliminary Results of Laboratory Tests

It is unnecessary to discuss the fact that modern views on the plasticization of rubber as well as the fundamental processes and methods involved, are not final and cannot pretend to an exhaustive solution of the problem. Nevertheless, despite the exceptional importance of these problems to the technology of rubber, they have not, in our opinion, attracted sufficient attention in the literature. Even less is found in the literature about the most recent methods of plasticization. This explains why in an investigation of the thermal plasticization of rubber which was begun by the authors in the early part of the current year, there was found to be little information in the literature. Only a few articles and reports indirectly related to the problem were available. Therefore we were compelled to spend considerable time in developing effective methods, and various experiments on the thermal vacuum treatment of rubber were carried out to ascertain the effect of the time, degree of vacuum, and temperature. Further experiments with and without a vacuum led finally to the method of treating rubber in heated air under pressure, with variations in the temperature, duration of treatment, and quantity of compressed air.

It should be noted that in all these thermal treatments, it was of great importance to expose the rubber under conditions which assured the maximum surface of contact. To this end we carried out a number of tests on the disintegration of rubber, and developed a method for obtaining it in a fine state of division with a treatment of only one minute. A definite weight of rubber was charged into a compensator and was run for one-half minute; after the addition of some water, the rubber was run for another one-half minute with the piston lowered. At the end of the operation, the disintegrated rubber was discharged in the usual manner. Even a prolonged treatment (up to 3 hours) at 140-150° C. gave no satisfactory indication of plasticization, and after 8-10 hours of rest all the samples showed plasticities by the Williams method of the order of 5.93, 5.81, 5.78, 5.61, 5.32, etc., compared with a mean plasticity before treatment of 6.71. The degree of recovery was 2.27, 2.99, 3.02, 2.26, 2.05. Moreover, in full agreement with the observations of Cotton and other investigators, all samples on subsequent rest lost their softness and gradually reverted to their original hardness.

An entirely different picture is revealed by the thermal treatment in air. These experiments confirm the views of Busse and Cotton on the function and importance of atmospheric oxygen in the mastication of rubber. Our tests were carried out in a laboratory pressure vulcanizer fitted with a jacket and a connection for introducing compressed air. A definite weight of disintegrated rubber in an iron wire basket was charged into the autoclave, previously heated to a desired temperature, and was heated at a definite temperature and time with passage of compressed air at a given rate. A sample treated in this manner was passed 3 or 4 times through a heated mill, and was tested after 10-15 hours of rest. Softening was found to proceed the more energetically and rapidly the greater the compression of the air and

the more frequent the replacement of the air. Excessive frequency of replacement may lead to a very considerable resinification of the rubber.

TABLE I
PLASTICITY BY THE WILLIAMS METHOD AND RECOVERY VALUES

Test	24. Hrs. after Treatment	After 2 Days	After 3 Days	After 5 Days	After 6 Days	After 8 Days
1	3.18-0.65	2.63-0.34	2.49-0.24	2.74-0.35	2.74-0.26	2.76-0.24
2	2.82-0.19	2.59-0.36	2.8-0.41	2.88-0.43	2.85-0.37	2.87-0.45
3	2.77-0.36	2.66-0.37	2.51-0.29	2.89-0.33	3.89-0.41	3.11-0.43
4	3.31-0.67	3.23-0.57	3.16-0.45	3.26-0.54	3.48-0.65	3.45-0.52

Experiments in which rubber was plasticized under approximately 3-3.5 atmospheres of air pressure at 140° for 1 and 1.5 hours showed the following plasticity (Williams) and recovery values, which remained unchanged after 4-6 days of rest: 3.9-0.8, 3.8-0.69, 3.15-0.5, 3.89-0.64, 3.58-0.42, 3.18-0.34, 2.9-0.38, 3.46-0.44, 2.95-0.37, 2.94-0.36, etc. These results are related to the experiments conducted under different conditions of air pressure and duration of treatment. The above data are related to the experiments carried out under very similar conditions (Table I).

TABLE II

Sample	Vulcanization Time (Min.)	Modulus at		Resistance to Tearing (Kg. per Sq. Cm.)	Relative Elongation (in Per Cent)	Residual Elongation (in Per Cent)	Hardness (by Shore Method)
		300%	500%				
Mixture with rubber, thermally treated, with plasticity 3.18	30	63.5	143.5	203	617	35	51
	45	66	148	188	590	32	52
	60	65.5	140	178	583	33	52
	75	62.5	132.5	158	563	29	53
Mixture with rubber, plasticized in the usual manner, with plasticity 3.55	30	73.3	172	192.5	537	43	57
	45	95	175	175	500	36	60
	60	97.5	...	129	383	23	60
	75	94.5	...	122	380	17	61
Mixture with rubber, thermally treated, with plasticity 3.15	30	68	154	185	567	31	59
	45	68	440.5(?)	180	580	31	51
	60	64	132	178.5	543	26	51
	75	69.5	135.5	148.5	537	25	50
Plasticization for 27 min., with plasticity 2.87	30	70	157.5	186.5	563	33	50
	45	66.5	146	172	553	32	51
	60	71	140.5	157	550	29	52
	75	67.5	139	157	533	25	50

In conclusion it seems desirable to present the results of physico-mechanical tests of several similar mixtures of rubber plasticized in the usual manner and by thermal treatment (Table II).

The problem of thermal plasticization cannot be considered to be solved. Nevertheless the results of the present investigation furnish the basis for at least two conclusions: 1. Thermal plasticization merits attention and should be utilized in the rubber industry. 2. Thermal plasticization may prove to be profitable also in connection with the existing method of mastication.

Investigations of Dispersing Agents and Stabilizing Agents for Latex Mixtures, and the Behavior of Latex Mixtures When Stored

Otto Bächle

RESEARCH LABORATORY OF THE RUBBER DIVISION OF THE I. G. FARBENINDUSTRIE A.-G.,
LEVERKUSEN, GERMANY

The great sensitivity to mechanical as well as to chemical influences which is possessed by latex, in common with all hydrophobic colloids, leads to immediate difficulties in the preparation of its mixtures. The ingredients, which in most cases are insoluble in water, must first be finely ground and then dispersed in water before being added to the latex mixture. Good dispersion is effected only by the use of high efficiency mechanical dispersion apparatus (ball mill, pigment grinding mill, etc.) and at the same time by the use of a suitable dispersing agent. Moreover, since latex mixtures may have to be stored for a long time, and since premature coagulation may take place during the preparation of such mixtures by the ingredients added or by mechanical influences, and later by incipient vulcanization, it is necessary to stabilize these latex mixtures in practice so that they can be handled safely. Much work has already been done on the stabilization of latex and latex mixtures, as a result of which a great number of products are recommended and used today. A certain stabilizing action is obtained by the addition of water, a greater stabilizing action by aqueous solutions of alkalies. Furthermore, soaps and soap-like compounds are used, *e. g.*, casein is in general a good medium. A few special products are offered today by the chemical industry.

Only very recently has there been interest in obtaining dispersions which are as nearly complete as possible and in every way satisfactory. Recently a few products have appeared on the market which are said to assist dispersion.

It would simplify the work of the latex technologist, if it were possible, to combine the dispersing and stabilizing actions in a single substance. We undertook the task of examining a large number of substances which seemed to be suitable for dispersion and stabilization, and of trying to find among them substances which have to an equal extent the power of dispersing the added ingredients and of stabilizing the resulting mixture. In order to approach this problem it was first necessary to develop suitable methods for testing the dispersing power and the stabilizing power.

1. *Dispersing Power.*—The particle size of active zinc oxide and Ultramicronex carbon black were determined by means of the Hahn method of sedimentation analysis in two-branched flocculation meters. These substances were dispersed in an aqueous solution of the dispersing medium under investigation. In addition, the dispersing power was measured colorimetrically by determining the degree of blackening of a latex mixture into which carbon black had been introduced after dispersion in the aqueous solution of the dispersing agent to be studied.

2. *Stabilizing Power.*—In an exact study of the stabilizing power, it was natural that the various causes of coagulation which played a part had to be distinguished

clearly. Every stabilizing agent was tested first as a protective against mechanical influences, such as stirring and agitation, secondly as a protective agent against heat, and third as a protective agent against the increase in viscosity and in most cases the subsequent coagulation of finished mixtures during storage.

With respect to the mechanical influences to which latex is exposed before use, it is protected sufficiently by the addition of alkalies, *e. g.*, ammonia. Ammonia and the natural protective agents which are present do not however have sufficient stabilizing power if the latex contains vulcanizing agents. Since the protection of untreated latex is of slight interest, the stabilizing agents were tested only in latex containing added ingredients. Latex was sensitized with Ultramiconex carbon black and with active zinc oxide in a series of parallel experiments. The testing of the stabilizing agents with this sensitized latex was carried out in the following manner. Ten grams of carbon black were ground 150 times in a mortar with 45 cubic centimeters of water and 0.5 gram of stabilizing agent, and 10 grams of zinc oxide were ground 150 times in a mortar with 25 cubic centimeters of water and 0.5 gram of stabilizing agent. Following this, the mixture was stirred into 80 cubic centimeters of a sixty per cent concentrate of latex in a 400 cubic centimeter beaker. After this addition was finished, the mixture was stirred with a glass rod 4.5 millimeters in diameter for 7 minutes with 200 revolutions per minute. Within 7 minutes partial coagulation had taken place. If after 7 minutes' stirring, this had not taken place, the mixture was then transferred to a 200-cc. wide mouthed bottle, and was agitated 180 times per minute until coagulation took place. The number of minutes (stirring index or agitation index) is a measure of the resistance to coagulation. With exact control of the experimental conditions, values were obtained which could be reproduced satisfactorily. In connection with the stability tests, it must be borne in mind that different supplies of latex vary in their stability, as well as in their ammonia content and their viscosity. All the experiments, in so far as they belong together, were always carried out with raw materials from the same supply.

The determination of the stabilizing power during heating was carried out with pure latex and also with sensitized latex. In this case also, Ultramiconex carbon black and active zinc oxide were used to make the latex sensitive. The latex and the latex mixtures containing carbon black and zinc oxide, to which the stabilizing agents had been added, were heated on an oil bath at 100° C. under constant experimental conditions. In order to prevent drying of the surface, a small jet of steam was passed over it. The mixtures were stirred carefully, observed continuously, and the length of time required for the first evidences of coagulation was determined.

The influence of stabilizing agents on the changes in the viscosity of latex mixtures upon storage was determined for complete latex mixtures with ultra-accelerators and with semi-ultra-accelerators by means of viscosity measurements.

The experiments described were carried out with a commercial sixty per cent concentrated latex which had been concentrated centrifugally. This latex concentrate contained, other than approximately 0.5 per cent of ammonia, no added protective agent, and was therefore suitable for testing stabilizing and dispersing agents, as well as for studies of finished latex mixtures, because no trouble was possible as a result of unknown impurities. All the results obtained apply to other types of latex.

Dispersion and Stabilization.—An examination of the results obtained during tests of the stabilizing and dispersing powers proved that the stabilizing and dispersing effects run counter to one another to a certain extent. In general the better the dispersion of the ingredients the less is the resistance to coagulation of the

latex mixture. A good dispersing agent for active zinc oxide or carbon black gives more sensitive latex dispersions if the conditions are kept constant (see Table I).

TABLE I

Stabilizing Agent	Relative	
	Dispersion	Stability
Glue	0	124 ×
Gelatin	0	108 ×
Water	1	100 ×
Turkey red oil	1	82 ×
Stabilizing agent X (commercial product)	1	80 ×
Emulphor FM	2	80 ×
Igepon T	3	30 ×
Casein	4	30 ×
Sodium oleate	4	6' 15"
Nekal BX	4	5' 40"
Pectin	6	5' 00"
Albumin decomposition products (sodium lysalbinat)	7	3' 04"

The Table shows the relative dispersion and stability of latex-carbon black mixtures which were prepared under similar conditions with various dispersing agents. The dispersion numbers were determined colorimetrically, and these

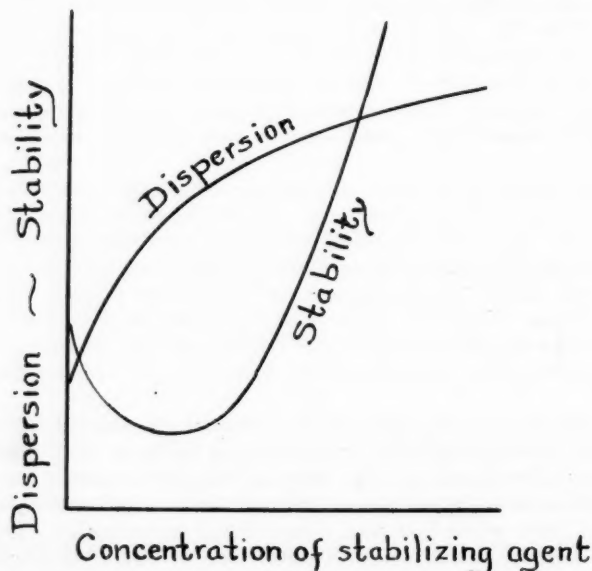


Figure 1

numerical values represent the relative degrees of blackening; 0 is the poorest dispersion; with increasing numerical values, blackening increases and accordingly the dispersion. Under relative stability are shown the stirring or agitation numbers, as determined by the method described earlier for testing the effects of stabilizing agents on coagulation brought about by mechanical causes.

It can be seen from the table that with increasing dispersion the stability diminishes. An explanation of this unfortunate dependence of the stabilizing effect upon the dispersing effect is simple—namely, the more finely divided the added substance, the greater is the surface effective for coagulation.

In studying the dependence of the stability and the dispersing effects on the concentration of the stabilizing agent, it was found that the dispersing action increased

TABLE II
Experiments with Gas Black

10 Per Cent Solution of Stabilizing Agent (in Cc.)	Water (a) Stabilizing Agent A	Relative	
		Dispersion	Stability
0	45.00	1	100 ×
0.05	44.95	1	90 ×
0.25	44.75	1	72 ×
0.50	44.50	1	47 ×
1.00	44.00	1	43 ×
2.50	42.50	2	40 ×
4.00	41.00	3	30 ×
5.00	40.00	4	35 ×
6.00	39.00	4	27 ×
7.00	38.00	5	34 ×
10.00	35.00	8	40 ×
15.00	30.00	8	330 ×

TABLE III
(b) Stabilizing Agent B

0.0	45.00	1	100 ×
0.05	44.95	1	90 ×
0.25	44.75	1	86 ×
0.50	44.50	2	84 ×
1.00	44.00	2	56 ×
2.50	42.50	3	43 ×
4.00	41.00	3	46 ×
5.00	40.00	4	47 ×
7.00	38.00	8	more than 2000 ×

with increasing concentration. The stability however, first diminished; therefore the latex mixture is more sensitive to coagulation, and only at higher concentrations of the stabilizing agent does the protective action appear. The graphical representation of the stability and dispersing power as functions of the concentration of stabilizing agents is shown in Fig. 1.

The abscissa represents the concentration of the stabilizing agent; the ordinate, the stability and dispersion. The relations shown were determined and confirmed with a series of stabilizing and dispersing agents. The results of a number of measurements of the dependence of the dispersion and the stability upon the concentration of stabilizing agents in latex mixtures, which were sensitized both with carbon black and with active zinc oxide, are summarized in Tables II to VI.

Each of these tables give the dispersion and stability values which were obtained with the different substances in latex mixtures containing carbon black and active zinc oxide, with increasing concentrations of stabilizing agents. With increase in the dispersion, there was in all cases first a decrease and then a rapid increase in the stability. Only such substances as have no, or only a slight, dispersing power

are exceptions to this behavior, for example, gelatin and glue. This dependence of the stability upon the concentration of stabilizing agents may be explained in the following way. Small quantities of the stabilizing agents are completely adsorbed by the substances to be dispersed, and bring about only a finer dispersion; a protective influence cannot yet manifest itself. On the contrary, the surface which

TABLE IV
(c) Vultamol

0.0	45.00	1	100 X
0.05	44.95	1-2	44 X
0.25	44.75	2	38 X
0.50	44.50	3	33 X
1.00	44.00	5	5' 15"
2.50	42.50	7	3' 55"
4.00	41.00	8	30 X
5.00	40.00	8	150 X
6.00	39.00	8	275 X
7.00	38.00	8	482 X
7.50	37.50	8	900 X
10.00	35.00	9	more than 2160 X

TABLE V
Experiments with Active Zinc Oxide

10 Per Cent Solution of Stabilizing Agent (in Cc.)	Water	(a) Stabilizing Agent B	Dispersion	Relative Stabilizing Power
0.0	25.00			30 X
0.05	24.96			39 X
0.25	24.75			3' 45"
0.50	24.50			3' 55"
1.00	23.00			4'
2.50	22.50		increasing dispersion	3' 10"
4.00	21.00			1' 35"
5.00	20.00			1' 10"
6.00	19.00			45"
7.00	18.00			25"
7.50	17.50			50"
10.00	15.00			45"
15.00	10.00			1' 20"
20.00	5.00			7'
25.00	0.00			172 X

is active toward the latex is increased by the better dispersion, and in this way there is at first an increased tendency to coagulate. Only when the filler has become saturated with the stabilizing agent can further additions exert their stabilizing influence. This effect increases rapidly with increasing concentration. It follows therefore that for good dispersion and at the same time good resistance to coagulation, the lowest concentrations of stabilizing agents must be used, which, as is evident from the facts described above, depend on the kind and quantity of the substances to be added.

In extensive comparative experiments with a large number of dispersing and stabilizing agents, it was found that Vultamol, the sodium salt of an organic thio acid, best combined the dispersing and stabilizing effects against mechanical influences. Therefore, for example, under the same conditions as in the experiment shown in Table I, the carbon black dispersion number equalled 8 with Vulta-

mol and the agitation number was 150 \times . The good dispersing power of Vultamol for carbon black compared with that of water and casein solutions can be illustrated as follows: Twenty grams of Ultramiconex carbon black were dispersed with

1. 90 cc. distilled water
2. 80 cc. distilled water + 10 cc. of a 10 per cent casein solution
3. 80 cc. distilled water + 10 cc. of a 10 per cent Vultamol solution

and stirred into 160 cubic centimeters of a 60 per cent latex concentrate.

The dispersing powers of the various dispersing agents are judged by the different degrees of blackening, *i. e.*, the deeper the color the better the dispersing power.

The dispersing influence on other vulcanizing agents and fillers like zinc oxide is also excellent.

Good dispersing power and stabilizing power toward mechanical influences are, as has already been pointed out, not the only properties which a preparation must have to be generally useful. The stabilization must also include stabilizing of the viscosity during storage, which often increases as a result of incipient vulcaniza-

TABLE VI
(b) Vultamol

0.0	25.00		30 \times
0.05	24.95		26 \times
0.25	24.75		23 \times
0.50	24.50		14 \times
1.00	24.00	increasing	7 \times
2.50	22.50	dispersion	30 \times
4.00	21.00		135 \times
5.00	20.00		1100 \times
6.00	19.00		1200 \times
7.00	18.00		1500 \times
10.00	15.00		1800 \times
15.00	10.00		more than 2160 \times

tion, without any influence on this incipient vulcanization by the stabilizing agent itself, either through activation or retardation. The stabilizing agents which we studied were also tested for their properties in this respect. The viscosities of latex mixtures, which depend upon the incipient vulcanization, were determined at regular time intervals for the various stabilizing agents. In addition the incipient vulcanization of latex mixtures was ascertained first by swelling experiments with small test-pieces which were prepared from the mixture to be tested, and secondly by testing the mechanical properties of test-rings which were prepared according to a special method from the latex mixtures being studied.

Besides its effect on vulcanization, a dispersing and stabilizing agent should naturally have no harmful effect on the aging and other properties of a vulcanizate.

It is further required of a good dispersing agent that it give a thinly liquid dispersion and that it make possible a minimum of liquid in rubbing together the components of the mixture and the shortest drying time for the product made from the latex mixture. Dispersing and stabilizing agents for latex mixtures should not have a tendency to foam, and they or their aqueous solutions must therefore have the highest possible surface tension. With the use of such a solvent the bubbles of air which are formed during the process of dispersion are not stabilized, but quickly burst when they come to the surface of the mixture.

As has already been pointed out, a test was carried out with the dispersing and

stabilizing agents on the stability toward the effect of heat. A dispersing and stabilizing agent for general use should not stabilize against the action of heat, for otherwise it would be no longer possible to use it in mixtures which are sensitized to heat.

Finally a stabilizing agent should not cause putrefaction and mold, as do some other organic substances.

Account would have to be taken to the greatest possible extent of these widely different requirements, in the development of a dispersing and stabilizing agent for latex mixtures.

The Use of Dispersing and Stabilizing Agents

After being wetted with an aqueous solution of the dispersing agent, the vulcanizing agents and the fillers were suitably ground in a pigment mill or in a ball mill,

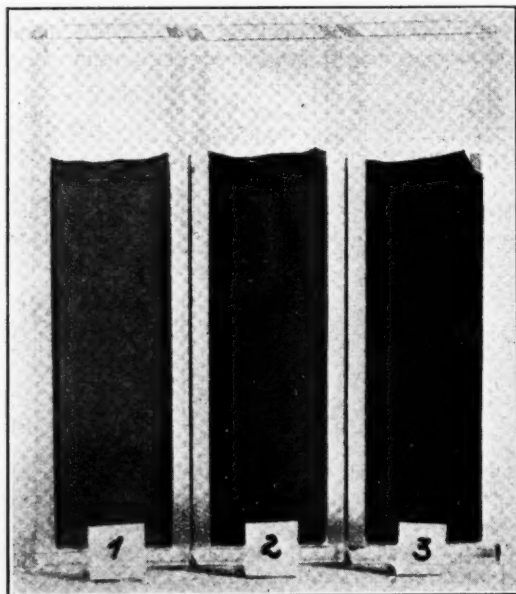


Figure 2

and the dispersion obtained was mixed with the latex. The aid of a mechanical pulverizing machine like the ball mill or the pigment mill is still necessary in spite of the good dispersing properties of a dispersing agent. Although the primary particles of the substance to be dispersed may be made very small by premilling or by means of a precipitation process, for the most part they still adhere so firmly together that it is almost impossible to separate them without mechanical treatment. In other cases the primary particles are still so large that it is necessary to pulverize them first by some grinding process. A good dispersing agent assists the action of the mill extraordinarily and, what is of more importance, prevents subsequent aggregation. Good dispersing agents make it possible to utilize to the fullest extent an efficient grinding process.

For the further utilization of a dispersing and stabilizing agent like Vultamol

the following directions may be given. In the preparation of unloaded mixtures, approximately 5 parts of a 10 per cent aqueous solution of the dispersing agent (based on 100 parts of dry rubber) are used. Such a mixture usually contains about 0.5–1.0 part of accelerator, 1.0–3.0 parts of sulfur and 0.8–2.0 parts of zinc oxide. For loaded mixtures, 20–50 per cent of a 10 per cent solution (based on the mixture) is required.

If the quantity of liquid, in the form of an aqueous solution of the dispersing agent, is still not sufficient to give a satisfactory consistency to the dispersion in

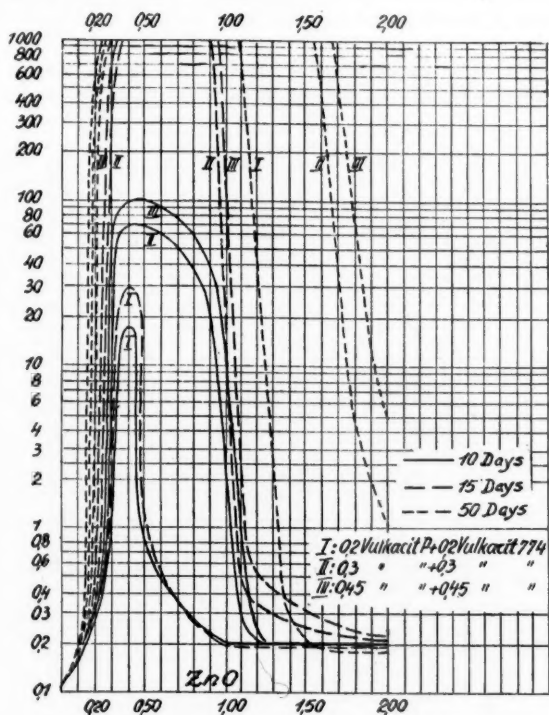


Figure 3

the grinding process, additional water is added so that the correct properties are obtained. Only soft water, or better, distilled water, is suitable for latex mixtures.

The Behavior of Latex Mixtures in Storage

Latex mixtures have a rather marked tendency toward incipient vulcanization. In practically all cases (it is hoped that exceptions may be reported later) incipient vulcanization takes place in aqueous dispersion, *i. e.*, in the presence of water, more rapidly than in a latex mixture from which the water has been removed by drying at room temperature. In a study of a large number of accelerators, it was proved that water-soluble accelerators in the presence of water frequently bring about incipient vulcanization relatively soon, whereas with water-insoluble accelerators such great differences are not seen in the incipient vulcanization of a latex mixture before and after drying. The zinc salts of dithiocarbamic acids behave relatively

well in this respect. The absolute rate of incipient vulcanization naturally depends upon the strength of the accelerator. The onset of vulcanization of mixtures with different accelerators was determined by the method already described above.

Incipient vulcanization of mixtures during storage precludes their further use or limits it to a certain degree, if, as is frequently the case, an increase in viscosity is associated with incipient vulcanization. As long as this does not take place, attention need be paid to the incipient vulcanization only in so far as shorter periods of heating are necessary and a decrease in tackiness results (which is of importance in the rubberizing of fabrics, etc.).

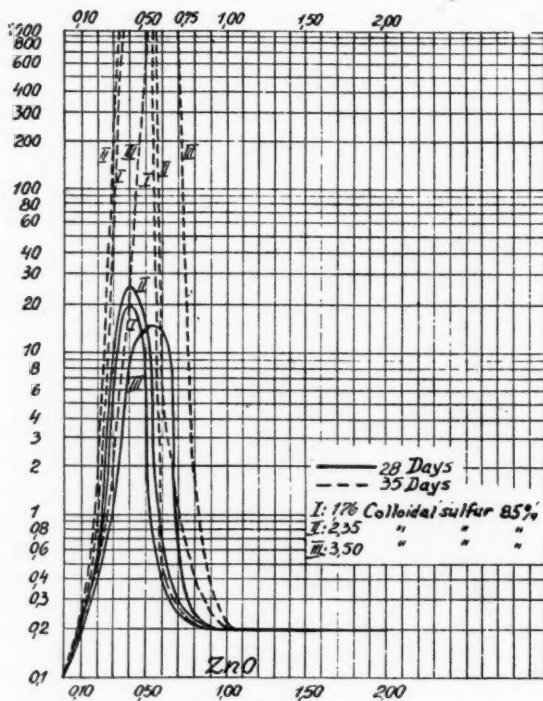


Figure 4

The increase in viscosity which frequently runs parallel with the beginning of vulcanization depends largely upon the composition of the mixture. Vultamol, for example, has a very favorable influence on the viscosity constant, and at the same time the addition of this ingredient does not influence in any way the beginning of vulcanization.

In the investigation of the influence of the different components of a mixture on the change in viscosity due to incipient vulcanization, particularly interesting observations were made on the influence of zinc oxide. It was found that with otherwise identical compositions of latex mixtures, those containing approximately 0.3–0.8 per cent of zinc oxide (based on the rubber) underwent the most rapid changes in viscosity during storage. This was seen in experiments with most widely different types of accelerators of both the ultra- and the semi-ultra

classes, and was also observed in experiments with different commercial grades of zinc oxide. The results of experiments with zinc oxide in the various proportions with which this phenomenon is most evident are shown in Fig. 3.

1. Mixture: 165.0 60% latex concentrate
 2.5 colloidal sulfur in pieces with 15% water
 5.0 a 10 per cent Vultamol solution
 0.5 Latekoll (thickening agent)
 - I. 0.20 Vulkacit P + 0.20 Vulkacit 774
 - II. 0.30 Vulkacit P + 0.30 Vulkacit 774
 - III. 0.45 Vulkacit P + 0.45 Vulkacit 774

In the three mixtures I, II, and III, with the various proportions of accelerator, active zinc oxide was varied, viz., 0.20, 0.40, 0.50, 0.60, 0.85, 1.00, 1.20, 1.50, and

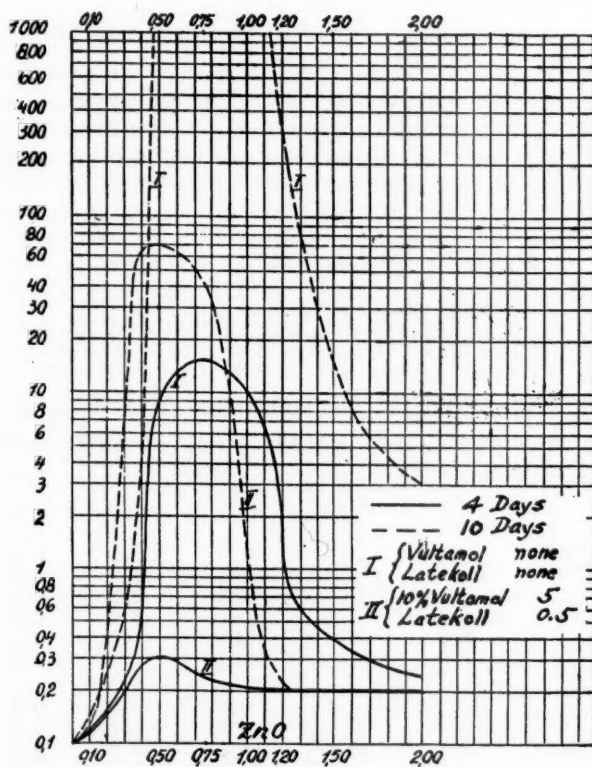


Figure 5

2.00. The viscosity of the mixtures was determined after 10, 15, and 50 days. The progress of the thickening is shown on the curves of Fig. 3.

The viscosity, which was determined by means of a viscometer constructed specially for this purpose, is represented on the ordinate as time (seconds), and with a logarithmic scale. The logarithmic scale was chosen because it permits a greater range of measurements. The abscissa represents the concentration of zinc oxide

(based on 100 parts of dry rubber). It can be seen that the thickening reached a maximum at approximately 0.4 part of active zinc oxide (per 100 parts of rubber), and was almost independent of the proportion of accelerator and the time of storage. With increasing quantities of accelerator and, as was to be expected, with the time of storage, the region of instability extended toward the direction of higher concentrations of zinc oxide.

The curves in Fig. 4 show the way in which the thickening of a mixture containing "Vulkacit P extra N" with increasing concentration of zinc oxide depends upon the proportion of sulfur.

2. Mixture: 165.0 60% concentrated latex
0.8 Vulkacit P extra N
5.0 10% solution of Vultamol
0.5 Latekoll

- I. 1.76 colloidal sulfur in pieces with 15% water
II. 2.35 colloidal sulfur in pieces with 15% water
III. 3.50 colloidal sulfur in pieces with 15% water

Active zinc oxide: 0.10, 0.25, 0.40, 0.50, 0.60, 0.75, 1.00, 1.20, 1.50, and 2.00.

In the mixture containing Vulkacit P extra N, the change in viscosity was likewise most rapid with approximately 0.4 per cent of active zinc oxide. The change in viscosity was almost independent of the proportion of sulfur. The range of instability at higher concentrations of sulfur increased very little.

That this change in the viscosity is not to be attributed especially to active zinc oxide is shown by the following experiments.

3. Mixture: 165.0 60% concentrated Latex
2.3 colloidal sulfur in pieces with 15% water
0.8 Vulkacit P extra N
5.0 10% Vultamol solution

- I. Active zinc oxide: 0.10, 0.25, 0.63, 1.60, 4.00, 10.00
II. RS zinc white: 0.10, 0.25, 0.63, 1.60, 4.00, 10.00
III. Special zinc oxide: 0.10, 0.25, 0.63, 1.60, 4.00, 10.00

The viscosity values of the mixtures with different types of zinc oxide at different concentrations after 2, 7, 14, 21, 28, and 35 days are shown in the following tables.

	Zinc Oxide					
	0.1	0.25	0.63	1.6	4.0	10.0
Active zinc oxide						
after 2 days	0.1	0.1	0.1	0.1	0.1	0.1
7 days	0.3	1.0	1.1	1.1	0.3	0.2
14 days	0.3	2.0	3.0	0.7	0.3	0.2
21 days	0.3	2.5	20.4	0.8	0.5	0.3
28 days	0.7	5.0	thick	1.0	0.5	0.4
35 days	0.8	7.2	thick	1.2	0.5	0.4
RS White zinc						
after 2 days	0.2	0.3	0.3	0.3	0.3	0.3
7 days	0.3	0.5	1.3	1.1	0.5	0.4
14 days	0.4	0.8	6.0	2.2	0.6	0.4
21 days	0.5	2.6	30.0	2.5	1.2	0.6
28 days	1.2	4.3	thick	14.1	1.8	1.0
35 days	1.4	5.5	thick	27.8	2.0	2.0
Special zinc oxide						
after 2 days	0.4	0.4	1.4	0.9	0.4	0.4
7 days	0.8	1.0	3.6	1.6	0.9	0.4
14 days	2.0	2.2	7.2	1.6	1.0	0.4
21 days	2.2	6.2	thick	1.6	1.0	0.4
28 days	2.2	11.4	thick	1.6	1.1	0.5
35 days	2.2	20.4	thick	1.8	1.1	0.5

The three experiments described (with Mixtures 1, 2, and 3) were carried out with mixtures containing Vultamol and in part Vultamol and Latekoll. A comparative experiment with a mixture without Vultamol and without Latekoll showed that mixtures without a stabilizing and thickening agent behaved qualitatively the same, whereas the changes in viscosity with all concentrations of zinc oxide commenced decidedly earlier. The changes in viscosity of a mixture such as:

165.00 60% concentrated Latex
 2.35 colloidal sulfur in pieces with 15% water
 0.30 Vulkacit P
 0.30 Vulkacit 774
 5.00 Water

and a similar mixture which, instead of 5.00 parts of water, contained 5.0 parts of a 10 per cent Vultamol solution and 0.5 part of Latekoll, with 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.75, 1.00, 1.20, 1.50, and 2.00 parts of active zinc oxide, gave the curves for a ten-day period shown in Fig. 5.

Both mixtures thickened most rapidly in the range of 0.3–1.0 part of zinc oxide, independent of the addition of Vultamol, while the mixture with Vultamol and Latekoll behaved essentially better.

The fact that more stable latex mixtures are obtained with increasing concentrations of zinc oxide appears at first to be at variance with the sensitivity of latex mentioned earlier. However, in this connection it should be noted that accompanying this sensitization by zinc oxide there is a diminution in the stability toward mechanical causes of coagulation; in the other cases, however, there is an improvement in the resistance toward the influence of incipient vulcanization.

In experiments which were designed to explain this surprising dependence of the changes in the viscosity of latex mixtures upon their zinc oxide contents, it was proved that this influence is not the result of incipient vulcanization, which depends in a corresponding way on the concentration of zinc oxide. It was found in all cases that the rate of vulcanization increased with an increasing content of zinc oxide.

Accordingly it is evident that, in addition to the choice of the correct stabilizing agent in the preparation of mixtures with constant viscosity, the correct choice of the concentration of zinc oxide is of decided importance.

Heat Capacity, Entropy, and Free Energy of Rubber Hydrocarbon

Norman Bekkedahl and Harry Matheson

Introduction

The best method for obtaining the free energy of formation of rubber is by making use of the third law of thermodynamics. This makes necessary the determination of heat-capacity values of rubber from room temperature down to temperatures sufficiently low to apply an empirical formula for obtaining the values below this lower temperature. From these heat-capacity values the entropy may be obtained. Then from this latter value, along with the entropy values of carbon (graphite) and gaseous hydrogen and the heat of formation of rubber, a reliable value for the free energy of formation of rubber may be calculated.

Several investigators have previously determined the heat capacities of rubber, but their observations were not made at temperatures sufficiently low to permit accurate extrapolation to the absolute zero in order to apply the third law. Furthermore, in the previous work the possibility that rubber at low temperatures might exist either as a metastable amorphous form or as a crystalline form was not clearly recognized. In the present investigation the aim was not only to extend the temperature range but also to obtain data of a higher order of accuracy than that previously reported.

Rubber Sample Investigated

The sample of rubber used in this investigation was prepared by the digestion of latex with steam at about 190° C., and the subsequent extraction of the resins and the products of hydrolysis with alcohol and water.²⁰ Where the term rubber or rubber hydrocarbon is used without qualification in this paper, the foregoing product is understood. The sample, of mass 38.30 grams, was cut into small pieces, roughly 10 cu. mm. each, before its introduction into the calorimeter. At that time it gave no indication of any oxidation having taken place. The air surrounding the rubber in the calorimeter container was replaced by helium so there would be no oxidation.

A complete set of values for the heat capacity of the amorphous form of rubber from 14° to 320° K. and several values for the crystalline form were obtained within the first several months. During this time the sample container of the calorimeter can remained gastight, and no oxidation of the rubber sample could have taken place. However, owing to a forced delay, no further measurements were made with the calorimeter for nearly two years, during which time the calorimeter can developed a leak and the helium was displaced by air. Oxidation of the sample was rapid, and by the time it was removed from the container it had a strong odor of oxidation products and had increased its weight to 39.38 grams. The increase in mass was about 2.8 per cent, and, if due to oxygen alone, would give an approximate empirical formula $C_5H_8O_{0.1}$ instead of C_5H_8 . During the several weeks previous to the removal of the sample from the calorimeter, a complete set of measurements was made on the crystalline form from 14° to 320° K., and several

measurements were repeated on the amorphous form. The air was pumped from the sample container during these observations so it was assumed that this final weight of the sample was constant during these later runs. The larger mass was used for the calculations of the results of the latter experiments while the original mass was used in the calculation of the results of the experiments performed two years before. When calculated in this manner the heat capacity of the rubber after this oxidation had occurred appeared unchanged within 0.2 per cent from its value before oxidation the results on both forms at different temperatures showing no consistent deviation from the earlier values. This seems to indicate that the oxidation had no significant effect on the value of the heat capacity of the rubber as determined in these experiments.*

It was not necessary to remove the sample from the container in order to convert it from one form to another. The procedure for obtaining the crystalline form of rubber was to cool the calorimeter to about -40°C . allow it to warm up slowly over a period of several days to 0°C ., and then to hold it at this latter temperature for several more days. Previous work** has indicated that this is sufficient time to obtain complete conversion into the crystalline form. Incomplete conversion would liberate heat in the temperature range from -40° to 0°C . which would easily be noticed from the behavior of the calorimeter during the heat-capacity measurements as was actually found to be the case on several occasions.

Calorimeter and Its Operation

The calorimeter used for the measurements of the heat capacities and the heat of transition was of the adiabatic and vacuum type described by Southard and Brickwedde³³ which is an improvement on the type originated by Eucken.³ The object of the vacuum surrounding the sample container is to minimize the exchange of heat between the container and its surroundings caused by gaseous conduction and convection. The calorimeter was made adiabatic by surrounding the sample container with a shield which, by means of controlled electrical heating, could be kept the same temperature as the sample thus minimizing heat leakages to and from the sample. The calorimeter is described in detail by Southard and Brickwedde, and only a few general statements need be made here. After the introduction of the sample into its container, the remaining air in the container was replaced by helium at about 1 atmosphere pressure before the container was sealed. Air could not be left inside because it would permit oxidation of the rubber, and also because it would liquefy at low temperatures. A vacuum in place of the helium would not be as suitable, because the lack of thermal conducting qualities would necessitate too long a time for the sample to reach temperature equilibrium, which was found to be the case in the latter experiments.

Measurements of temperature were made by means of a resistance thermometer of platinum containing 10 per cent of rhodium, the resistance of which was about 150 ohms at room temperature. From 14° to 90°K . its calibration was made against a helium gas thermometer described by Southard and Milner.³⁴ Above 90°K . it was calibrated against a standard platinum resistance thermometer in a precision cryostat designed and built by Scott and Brickwedde.³⁰ Resistances were measured by means of a Wenner potentiometer^{2,37}, potentials being obtained

* These results indicate, however, that at room temperature the oxygen taken up by the rubber must have a heat capacity contribution of about 7 calories per oxygen atom if the addition causes no change in the heat capacity per gram of total sample. This value of 7 calories is considerably larger than that usually derived from organic compounds by Kopp's rule.

** It is of interest to note here that from a calculation of the entropy of the rubber hydrocarbon at 298.1°K . from a table on page 210 of Parks and Huffman's "The Free Energy of Some Organic Compounds" (Chemical Catalog Co., Inc., New York, N. Y.), a value of $1.92\text{ J/g.}^{\circ}\text{C}$. is obtained. This assumes a long chain rubber molecule having 1 CH_2 branch chain and 1 double bond per C_6H_8 unit.

across the thermometer and also across a 100-ohm standard coil in series with the thermometer when a current of about 1 milliampere was passing through the circuit. This current was supplied by a 2-volt lead storage battery. The pre-

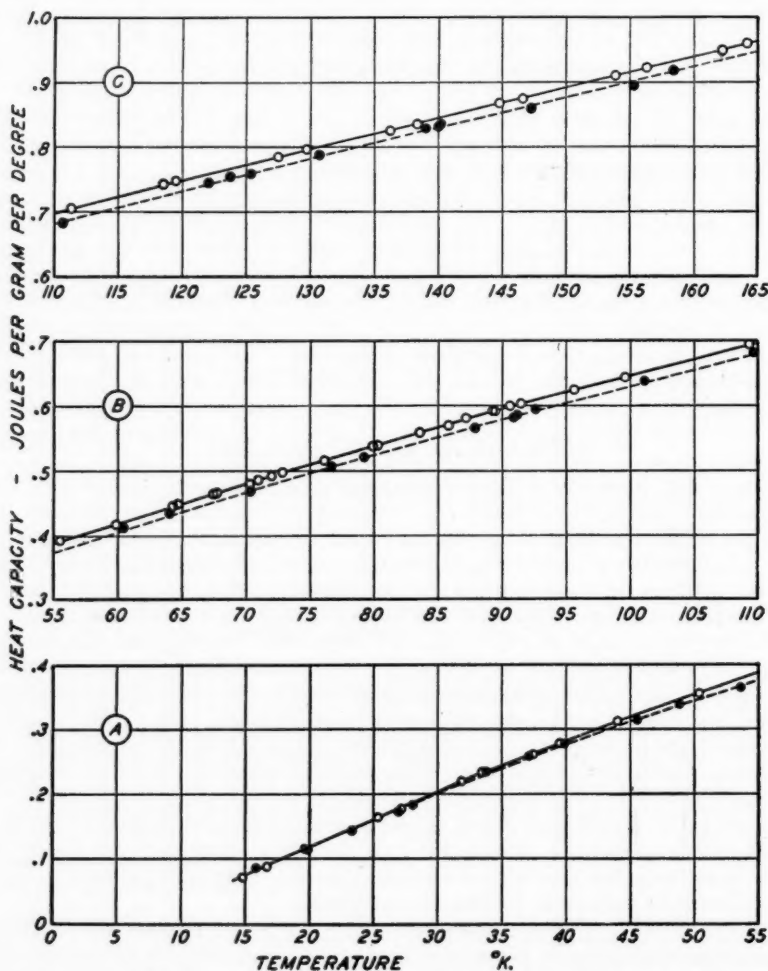


Figure 1—Relation between Heat Capacity of Rubber Hydrocarbon and Temperature

The dotted line represents the crystalline form and the solid line the amorphous. (See Fig. 2 for other half of curve.)

cision of the temperature measurements was within 0.002°C. above 90°K. and within 0.01°C. at lower temperatures.

This thermometer was also used as a heater. The current and voltage during the heating were also measured with the same potentiometer, using a 1-ohm standard resistance coil and a volt-box with a ratio of 150:1. Lead storage cells of 120 volts were the source of the heating current. The time of heating was regulated

by an automatic switch connected to time signals, which gave a measure of time to within 0.01 second. The time of heating was varied from 5 to 30 minutes, the heating current from 0.03 to 0.1 ampere, and the temperature from 0.5 to about 15° C. The amount of heat added could be measured to within 1 part in 10,000,

TABLE I
HEAT CAPACITIES OF THE RUBBER HYDROCARBON

Form of the Rubber Hydrocarbon			Form of the Rubber Hydrocarbon		
Temperature ° K.	Crystalline j/g./° C.	Amorphous j/g./° C.	Temperature ° K.	Crystalline j/g./° C.	Amorphous j/g./° C.
15	0.073	0.073	175	0.995	1.009
20	0.117	0.117	180	1.018	1.032
25	0.161	0.161	185	1.041	1.054
30	0.202	0.204			
35	0.240	0.243	190	1.064	1.078
			195	1.086	1.102
40	0.276	0.282	200	1.200	1.440
45	0.310	0.317	205	1.397	1.603
50	0.343	0.352	210	1.474	1.615
55	0.374	0.387			
60	0.405	0.418	215	1.506	1.628
			220	1.534	1.641
65	0.437	0.450	225	1.560	1.655
70	0.467	0.480	230	1.587	1.668
75	0.497	0.510	235	1.616	1.682
80	0.524	0.537			
85	0.552	0.566	240	1.644	1.696
			245	1.664	1.710
90	0.579	0.596	250	1.684	1.723
95	0.605	0.622	255	1.704	1.737
100	0.629	0.646	260	1.723	1.750
105	0.656	0.673			
110	0.681	0.697	265	1.743	1.764
			270	1.763	1.777
115	0.707	0.723	275	1.783	1.790
120	0.733	0.748	280	1.804	1.805
125	0.757	0.772	284 ^a	(^a)	(^a)
130	0.781	0.796			
135	0.805	0.820	285	...	1.822
			290	...	1.840
140	0.829	0.844	295	...	1.865
145	0.853	0.868	300	...	1.890
150	0.877	0.892	305	...	1.915
155	0.901	0.916			
160	0.925	0.939	310	...	1.940
			315	...	1.965
165	0.948	0.963	320	...	1.990
170	0.972	0.986			

^a Heat of fusion at 284° K. is 16.7 j/g.

which is greater precision than is necessary, since the temperature rise could sometimes be measured only to about 1 part in 1000. It was not found difficult to control the shields so that the sample would remain constant in temperature within 0.002° C. for an hour, even when its temperature was many degrees above that of the surrounding external bath. An actual test of the heat exchange to and from the sample was made with an external bath of liquid hydrogen at about 20° K., the sample and its container at about 90° K., with the shields a little more than a degree higher. Here the temperature of the sample rose 0.15° C. per hour.

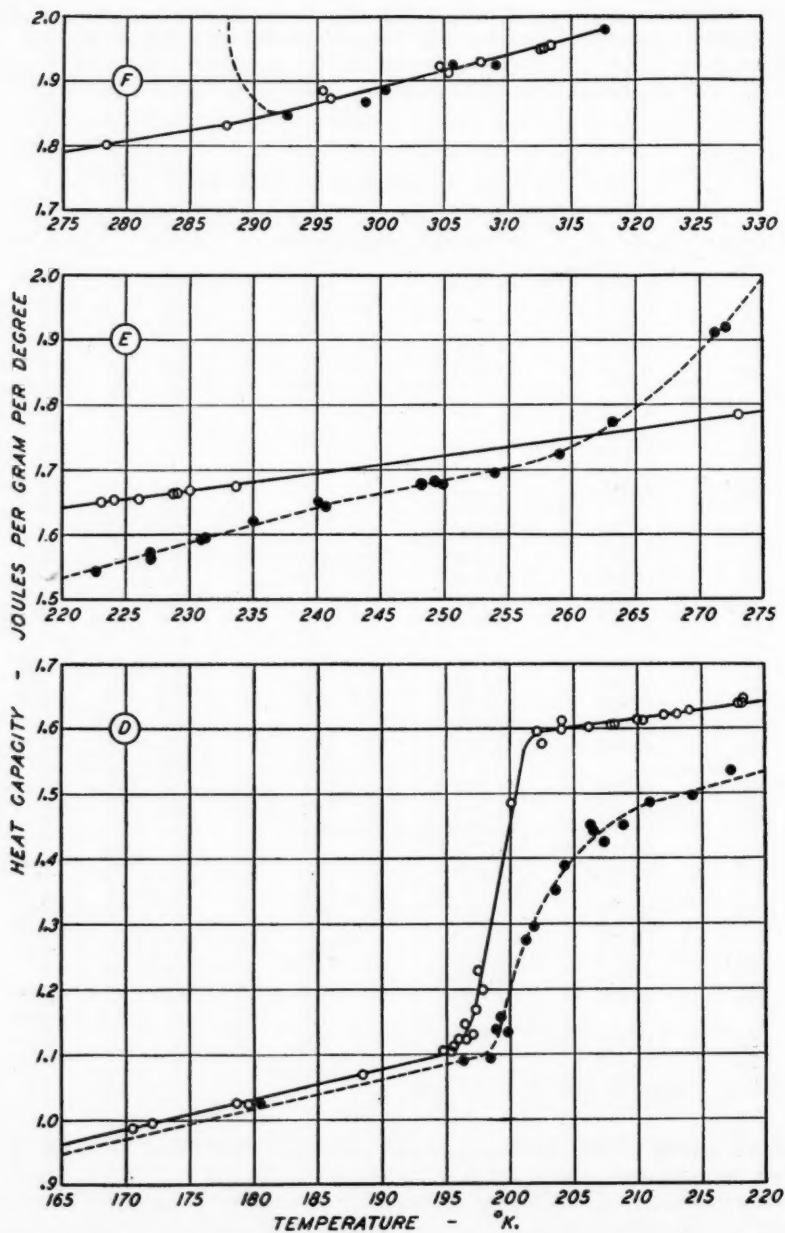


Figure 2—Relation between Heat Capacity of Rubber Hydrocarbon and Temperature

The dotted line represents the crystalline form and the solid line the amorphous. (See Fig. 1 for other half of curve.)

With the shields only 0.4°C . higher, the rate of temperature rise was 0.04°C . per hour. In actual operation of the calorimeter, the temperature of the shields was kept within 0.01°C . of that of the sample, and these deviations were not consistent in either direction, but tended to balance each other.

Two operators were necessary for conducting experiments with the calorimeter.

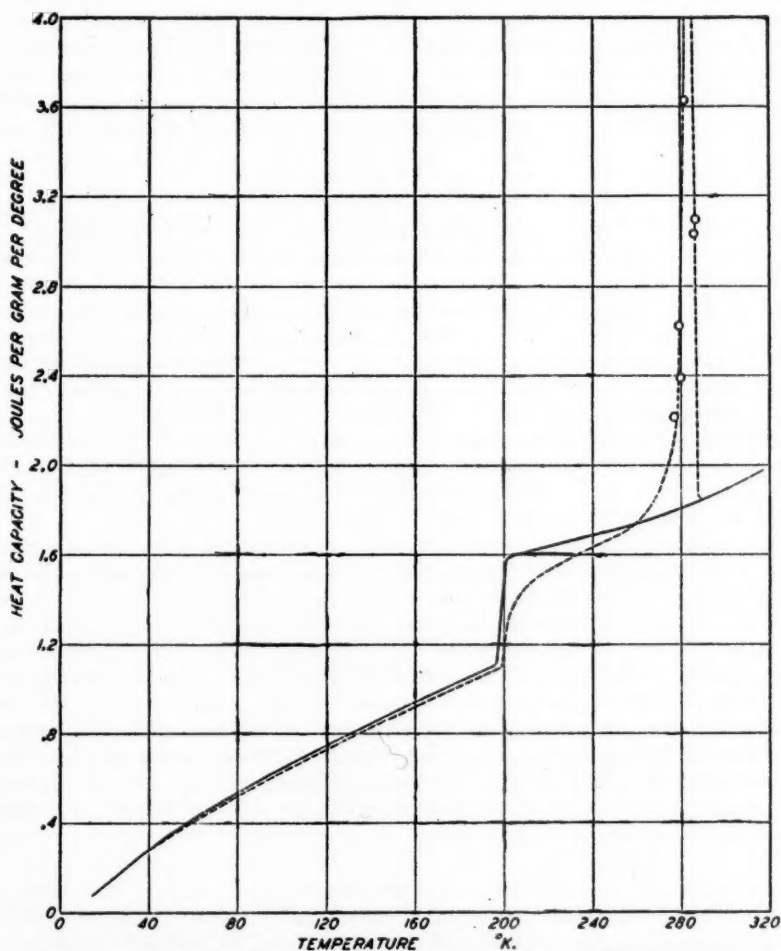


Figure 3—Relation between Heat Capacity of Rubber Hydrocarbon and Temperature

The dotted line represents the crystalline form and the solid line the amorphous.

One made the measurements on the temperature of and the heat energy added to the sample and container, while the other controlled the temperatures of the shields. The latter was done by regulating the current flowing through the heating wires of the shields. After the sample had shown a constant temperature over a period of several minutes, the electrical switch was thrown for the addition of heat. This necessitated a corresponding increase in the quantity of heat to the shields

in order to maintain them at the temperature of the sample. The heat to the shields, of course, was not measured. The heat delivered to the sample was determined from current and voltage readings made at definite time intervals. When the heating interval was complete, the automatic switch was again thrown, this time to stop the heating current. When temperature equilibrium was again established, which generally took from 5 to 10 minutes, the temperature was again measured, and then another heating period started. During these heating periods resistances of the current leads from the heater to the shield were measured. The assumption was made that one-half the heat produced in these leads went to the sample and container and the other half to the shields. Corrections for this additional current were found to be about 3 parts in 10,000 at room temperature and less at lower temperatures.

Heat Capacities

The curves in Figs. 1 and 2 give the relation between heat capacity and temperature, the solid line indicating the amorphous form of rubber and the broken line the crystalline form. The curve is shown in sections so that a larger scale may be used. Figure 3 gives the same curves on a smaller scale, the only points of observation shown being those in the transition range, which are not indicated in Figs. 1 and 2 because of the scale used. Table I gives the heat-capacity values at 5° intervals obtained from the curve. All quantities of heat in this paper are expressed in international joules. The factor for conversion into cal.₁₅ is 4.1833.²⁵

With the exception of the range of temperature where the crystals are melting, the heat capacities of the crystalline form of rubber are in general lower than those of the amorphous form. This is to be expected because of less randomness of the positions of the molecules in the crystalline form.

Tables II and III give the data and results of the calculation of one observation on the heat capacity of the crystalline form of the rubber hydrocarbon. Current reversals were made and the values obtained in the two directions were averaged in order to compensate for any stray currents which may have been present in the system. The mean temperature and the rise in temperature were obtained directly from the data in Table II. In order to obtain the amount of heat added, the values of the current passing through the heater and also the potential across the heater (Table III) were plotted as a function of time, and the values at the half-period of heating (6.5 minutes) were taken as the average. Both the current and the voltage show straight-line relationships with time over short intervals such as this unless the sample is undergoing a transition, in which case there will appear a change of slope of the voltage curve with time.

TABLE II
MEASUREMENTS OF TEMPERATURE BEFORE AND AFTER HEATING

Potential Measurements Across				Temperature of Sample		
100-Ohm Re- sistance	Thermome- ter	Direction of Thermome- ter Current	Current in Thermometer	Resistance of Ther- mometer	Before Heating	After Heating
<i>Volt</i>	<i>Volt</i>		<i>Ampere</i>	<i>Ohms</i>	<i>°K.</i>	<i>°K.</i>
0.0999995	0.0889020	Normal	0.000999995	88.9024	65.662
0.0999990	0.0889012	Reverse	0.000999990	88.9020		
0.1000145	0.0915000	Normal	0.001000145	91.4867	74.900
0.1000145	0.0914975	Reverse	0.001000145	91.4843		
Mean temperature					70.281° K.	
Rise in temperature					9.238° K.	

TABLE III
MEASUREMENT OF HEAT ADDED

Time Minutes	Potential Measure- ments Across		Direction of Battery Current to Potentiometer	Current in Heater Amperes	Potential Across Heater Volt
	1-Ohm Resistance Volt	Volt-Box Volt			
0 (begin)
1	0.058393	Normal	0.058393
2	0.058393	Reverse	0.058393
3	0.034657	Normal	5.1989
4	0.034729	Reverse	5.2097
5	0.058374	Normal	0.058374
6	0.058374	Reverse	0.058374
7	0.034938	Normal	5.2410
8	0.035006	Reverse	5.2512
9	0.058355	Normal	0.058355
10	0.058353	Reverse	0.058353
11	0.035217	Normal	5.2829
12	0.035283	Reverse	5.2928
13 (end)
Mean values (from curve)				0.058370	5.2355
Current through the 3000-ohm volt-box				0.001745
Current through the heater				0.056625
Time of heating, seconds					780
Total heat added, joules					230.46
Heat added, j/° C.					24.95
Heat absorbed by empty calorimeter, j/° C.					6.45
Heat absorbed by 39.38 grams of sample, j/° C.					18.50
Heat capacity of sample at 70.28° K., j/g./° C.					0.4698

Previous investigators have determined the heat capacities of rubber with various results. Gee and Terry⁹ were probably the first to measure the specific heat and obtained a mean value of 2.00 j/g./° C. on raw rubber between about 20° and 100° C. This compares fairly favorably with the results at the higher temperatures obtained in the present investigation. LeBlanc and Kröger¹⁹ made measurements from -70° to +40° C. on various samples of smoked sheet rubber. While not very smooth in most cases, their curves gave an average value of about 2.2 j/g./° C. at 25° C., which is considerably higher than the value 1.88 indicated in Fig. 2. Ruhemann and Simon²⁹ obtained a value of about 2.1 j/g./° C. for smoked sheet at 25° C. Boström⁵ reported an average value of 1.55 j/g./° C. at 17° C., which is lower than the 1.85 value obtained in the present investigation. Ruhemann and Simon's value for the specific heat at -80° C. was about 1.2 j/g./° C. as compared with 1.09 for that temperature as indicated in Fig. 2. In an earlier investigation on the heat of vulcanization of rubber²¹, mean heat-capacity values were obtained between 25° and 175° C. The average mean value obtained for both crude and purified rubber was 2.17 j/g./° C., which seems quite reasonable from the trend of the curve of the present investigation.

The curve obtained by Ruhemann and Simon for the heat capacities of smoked sheet from -100° to about -20° C., which includes a transition of the second order,^{3,7} which they called the α anomaly, is similar to the one obtained in the present investigation. At 0° C. they obtained a hump in the curve which they called the β anomaly, but this break in the curve could not be found in the present investigation. Figure 3 shows that at 284° K. a transition of the first order takes place in which there is melting of rubber crystals. This transition was named the

γ anomaly by Ruhemann and Simon, but was found by them to take place at a temperature several degrees higher.

The transition obtained at 199° K. in this investigation is probably the same as that shown in some previous work on the thermal expansion and dielectric constant of rubber,³ and there reported to take place at approximately 200° K. The temperature of fusion obtained in the present investigation also agrees with that obtained from data on the coefficient of thermal expansion.

Heat of Fusion

At above 255° K. the curve for the heat capacity of the crystalline form begins to rise, owing to the premelting of some of the crystals. Although the fusion temperature is 284° K., there is a great tendency for the rubber to premelt with respect to the average temperature of the calorimeter. The higher local temperature near the heating coil produces a small amount of melting, which does not reverse itself when temperature equilibrium is established below the fusion temperature, because the rate of transition from the crystalline to the amorphous form is much greater than that in the reverse direction.³ This, however, will have no appreciable effect on the value obtained for the heat of melting.

With the rubber in the crystalline form, a heating was begun at a temperature of 253.73° K., continued through the transition, and ended with an equilibrium temperature of 291.90° K. The heat required to raise the rubber through this temperature range was 102.605 j/g. On the heat capacity-temperature diagram, a smooth curve was drawn from some point on the curve of the crystalline form just below the beginning of the melting of the rubber (about 250° K.) to the curve above the temperature of the transition. The energy required to bring the rubber from 253.73 to 291.90° K., assuming no transition, was obtained by measuring the area under this curve between these two temperatures, and was found to be 85.894 j/g. The difference between these two energy values in 16.71 j/g., which is the heat of fusion of the rubber. This value is in agreement with that obtained in a similar manner by Ruhemann and Simon²⁹ for frozen smoked sheet. Van Rossem and Loticius³⁰ report a value of 21.1 j/g. for latex sheet at 0° C., obtained from the difference between the heats of swelling of frozen and thawed rubber.

Entropy

According to the third law of thermodynamics, the entropy of a substance in the liquid state at 298.1° K. is given by the Equation

$$S_{298.1}^0 = \int_0^{T_{mp}} C_p(\text{crystals}) d\ln T + \frac{\Delta H_{\text{fusion}}}{T_{mp}} + \int_{T_{mp}}^{298.1} C_p(\text{liquid}) d\ln T$$

Curves were prepared plotting the values of the heat capacities at constant pressure, C_p , of the rubber hydrocarbon, both in the crystalline and the amorphous forms, as functions of the logarithm of the absolute temperature T . Since C_p values were obtained only as low as 14° K., the graphic integration of these curves could not be made below this point. Here the Debye approximation formula⁶ was used. From tables³¹ of the heat capacities and Debye functions, $\beta\nu$, the latter was found to be constant with a value of 120 from 14° to 35° K. From tables³¹ of the Debye functions and entropies with a $\beta\nu$ value of 120, the entropy change of the rubber from 0° to 14° K., $\int_0^{14} C_p d\ln T$, was found to be 0.015 ± 0.001 j/g./° C. for both the amorphous and the crystalline forms.

From the graphic integration of the curves the following values were obtained.

$$\int_{14}^{298.1} C_p d \ln T \text{ (amorphous form)} = 1.860 \text{ j/g./}^\circ \text{C.}$$

$$\int_{14}^{284} C_p d \ln T \text{ (crystalline form)} = 1.717 \text{ j/g./}^\circ \text{C.}$$

$$\int_{284}^{298.1} C_p d \ln T \text{ (amorphous form)} = 0.090 \text{ j/g./}^\circ \text{C.}$$

The entropy of fusion of the crystalline form of rubber at 284° K.,

$$\frac{\Delta H_{284}(\text{fusion})}{T} = 0.059 \text{ j/g./}^\circ \text{C.}$$

Following the curve for the amorphous form, one obtains

$$S_{298.1} - S_0 = \int_0^{14} C_p d \ln T + \int_{14}^{298.1} C_p d \ln T = 1.875 \pm 0.004 \text{ j/g./}^\circ \text{C.}$$

From the data on the crystalline form one obtains

$$S_{298.1} - S_0 = \int_0^{14} C_p d \ln T + \int_{14}^{284} C_p d \ln T + \frac{\Delta H_{284}(\text{fusion})}{T} + \int_{284}^{298.1} C_p d \ln T = 1.881 \pm 0.010 \text{ j/g./}^\circ \text{C.}$$

The third law of thermodynamics states that a pure substance in the crystalline state has zero entropy at the absolute zero of temperature. Any other form may not have zero entropy, as has been found by several investigators.^{11,16,17,23,24,32} The entropy of rubber at 298.1° K. is obtained from the last equation by setting the entropy of the crystalline form equal to zero at 0° K. Then for rubber at 298.1° K., $S_{298.1} = 1.881 \pm 0.010 \text{ j/g./}^\circ \text{C.}^3$

The above data give for the difference between the entropies for the crystalline and amorphous forms at 0° K. the value $(1.881 \pm 0.010) - (1.875 \pm 0.004) = 0.006 \pm 0.011 \text{ j/g./}^\circ \text{C.}$ This indicates, within the accuracy of the present experimental data, that S_0 (amorphous) - S_0 (crystalline) is not greater than 0.017 j/g./° C., or 0.28 cal./° C./C₅H₈ unit.

Free Energy of Formation

Various investigators^{4,12,15,18,22,36} have determined the heat of combustion of rubber, but the results of Jessup and Cummings¹⁵ are probably the most nearly accurate. Their value for steam-purified rubber at 30° C. is $45,239 \pm 90 \text{ int. j/g.}$ Using the values of specific heats of 1.89 j/g./° C. for rubber at 27.5° C. as determined in this investigation, 8.9 cal./mole/° C. for CO₂,¹³ 7.0 cal./mole/° C. for O₂, and 17.5 cal./mole/° C. for H₂O,¹ the heat of combustion of the rubber hydrocarbon at 298.1° K. is calculated to be $45,250 \pm 90 \text{ int. j/g.}$

Using the heats of formation at 298.1° K. of gaseous CO₂ taken as $-94.24 \pm 0.10 \text{ kcal./mole}^{27,28}$ and of liquid H₂O $-68.313 \pm 0.010 \text{ kcal./mole},^{26}$ the heat of formation of the rubber from its elements, $\Delta H_{298.1}$ is $-507 \pm 100 \text{ j/g.}$ Likewise, from the entropies of carbon (graphite) taken as $1.36 \pm 0.03 \text{ cal./mole/}^\circ \text{C.}^{14}$ and H₂ $31.23 \pm 0.00 \text{ cal./mole/}^\circ \text{C.},^{10}$ the entropy of formation of the rubber hydrocarbon at 298.1° K., $\Delta S_{298.1}$, is $-6.215 \pm 0.014 \text{ j/g./}^\circ \text{C.}$ Then, from the thermodynamic formula $\Delta F = \Delta H - T\Delta S$, the thermodynamic potential or free energy of formation of the rubber hydrocarbon at 298.1° K., $\Delta F_{298.1} = (-507 \pm 100) -$

$(298.1)(-6.215 \pm 0.014) = 1345 \pm 100 \text{ j/g.}$, or $1.35 \pm 0.10 \text{ kj/g.}$, or $21.9 \pm 1.6 \text{ kcal./C}_5\text{H}_8 \text{ unit.}$

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Raman Spectrum of Rubber and Some Related Hydrocarbons

S. D. Gehman and H. J. Osterhof

The Raman spectra of organic compounds have been used very extensively in studying their structure and the method has been applied for the solution of some difficult problems of constitution. The extension to highly polymerized materials has been very limited, although it offers a means of gaining information about the primary chemical linkages without disturbing the secondary forces. Signer and Weiler¹ showed that polysterol gave a strong line spectrum in which the frequencies were practically identical with those of ethylbenzene, the unit of structure in the long chain molecules. They showed, furthermore, that the frequencies were the same in the solid state and in solution, for this polymer, indicating an independence from the micellar forces.

The Raman spectrum has not been used at all, previously, for the study of rubber or related high polymers, attempts to secure a line spectrum leading only to bands and background.^{2,3,4} The difficulties and ambiguities in the deduction of the original structure of rubber from chemical reactions should make welcome any insight which can be gained by the application of this newer method.

The Raman spectra of series of organic compounds show that certain frequencies can be ascribed to the various primary organic linkages. Some of these frequencies are remarkably independent of the rest of the structure of the molecule. This property renders possible the use of the Raman spectrum to study the primary linkages in highly polymerized materials, since the frequency will depend not upon the size of the molecule but upon the unit of structure. The various linkages can then be identified by comparison with those of simpler, related structures.

The results to be obtained from a study of the Raman spectra of such materials as rubber and its derivatives promise to be extremely interesting, but the work has been hampered by the presence of a continuous background which we have not been able to eliminate entirely. Signer and Weiler¹ have mentioned the possibility that each molecule of a high polymer possesses a fluorescent end group and have even suggested the measurement of the continuous background intensity as a means for estimating the average molecular size. They admitted, however, as an equally probable alternative, that the background might be caused by fluorescent impurities. It would be interesting to determine for rubber, with the fluorescence microscope, whether the fluorescence occurred in the sheath of the latex particle. Another difficulty encountered in this work is the almost necessary limitation of having to work with solutions and gels thus reducing the Raman intensities due to the dilution. Crystal powder methods⁵ might be applicable but they do not seem very promising unless the source of light is entirely free of a continuous spectrum.

Apparatus and Method

The apparatus was of the conventional type for Raman studies of liquids and is sketched in Figs. 1 and 2. The light source was a quartz mercury arc and the spectrograph a Bausch and Lomb No. 2700 constant deviation instrument. The cells were constructed from Pyrex tubing as shown in Fig. 1, having rubber packing at the ends overlaid with a thin coating of acid-proof cement. The arc was cooled by

a fan. The equipment was designed for continuous operation and exposure times varied from four to forty-eight hours. In practically all of the work, the filter was an alcoholic solution of Victoria blue dye, as recommended by Magat.⁶ It was absolutely necessary to exclude the ultra-violet light and this filter had the added advantage of reducing the intensity of the continuous spectrum from the arc since it transmits almost exclusively the 4358 Å. U. triplet. This simplifies the interpretation of the results. The filter necessitates much longer exposures than would otherwise be necessary.

Eastman Spectroscopic Plates, types I or II, usually with J green sensitization, were used. The plates were measured with a micrometer microscope especially adapted for use at low magnifications. A calibration curve was drawn for the instrument by measuring the distance of known Raman lines from the 4916 Å. U. mercury line. Unknown frequencies were then determined by measurement of their distance from this line, a type of procedure recommended by Kohlrausch⁵ (p. 43).

The rubber was diffusion rubber prepared by allowing acetone-extracted pale crepe to stand in contact with ethyl ether or petroleum ether for several weeks, precipitating the material in solution with acetone and drying in vacuum. The

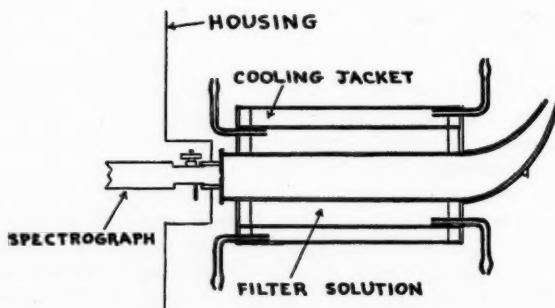


Figure 1

petroleum ether diffusion rubber gave a much clearer solution in carbon tetrachloride than the ethyl ether diffusion rubber and hence was preferable for this work. However, a mixture of carbon bisulfide and carbon tetrachloride having a refractive index about the same as that of rubber gave a very clear solution with the ethyl ether diffusion rubber so that Raman lines could readily be obtained with it. As it was desirable to obtain as clean and concentrated a solution as possible, the following technic was used in preparing the cells. The diffusion rubber was gathered up with a glass rod as it was precipitated and packed as tightly as possible into the cell. The cell was evacuated until the rubber was solvent-free and the window then sealed on with water-glass. This procedure reduces the handling of the rubber, and consequently the contamination with dust, to a minimum. The rubber was also sometimes dried, cut into small pieces and packed into the cell, being handled with glass rods and forceps. The solvent was introduced by connecting the horn of the cell first to a high vacuum pump and evacuating for several hours and then to a glass tube, the tip of which was broken under the solvent. The solvent flowed in and filled the cell. In this way, concentrations of rubber as high as 40% or more by volume could be obtained.

The balata was purified by dissolving the crude material in hot high test gasoline and, after standing overnight in a tall graduate, siphoning off the solution, and

centrifuging. It was precipitated by chilling, redissolved in hot petroleum ether, precipitated again by chilling, washed with acetone using a suction filter, and dried in vacuum. The cells were prepared in the same way as those for rubber.

Measurements

The Raman frequencies for rubber, balata, and myrcene are shown in Fig. 3 the height of the lines indicating the estimated relative intensities. The sample of

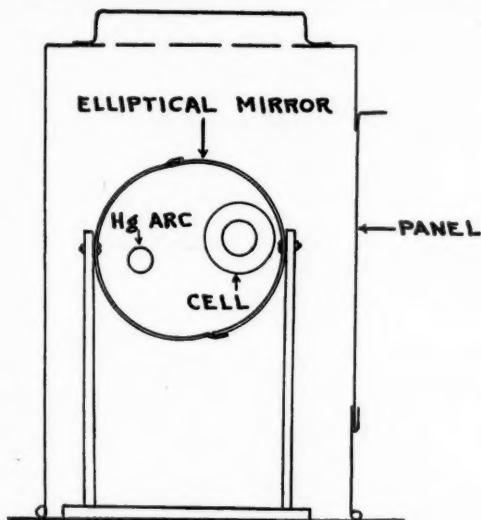


Figure 2

myrcene was very kindly supplied by Dr. S. Palkin of the Bureau of Chemistry and Soils.⁷ It was apparently very pure and showed little background. The lines for trimethylethylene, isoprene, and limonene were available in the literature,^{8,9,10,11} but these compounds were measured again to check our calibration.

Table I lists the frequencies for these hydrocarbons. The spectra for rubber and balata are still undoubtedly incomplete due to the obscuring of weak lines by the

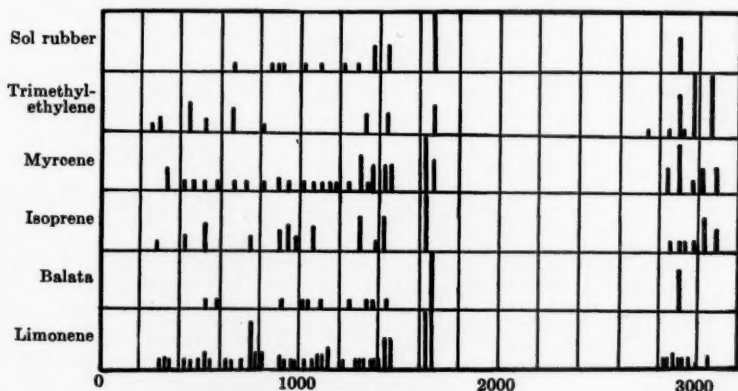


Figure 3

TABLE I

Raman Frequency	Intensity	Frequency ^a	Intensity	Frequency	Intensity
Isoprene ⁸		Trimethylethylene		Limonene ¹⁰	
286	2			308	1
428	3	253	1	330	2
529	6	389	3	350	1
778	3	444	7	432	2
901	5	528	5	471	1
952	6	767	6	491	2
992	3	803	1	524	4
1070	6	1338	4	545	2
1296	8	1446	4	639	2
1388	2	1679	7	662	1
1426	8	2732	1	702	2
1640	15	2861	1	757	10
2864	1	2885	10	790	4
2908	2	2922	1	800	4
2930	2	2973	15	895	3
2986	2	3055	15	918	2
3012	8			956	1
3090	5	Rubber		995	1
		402	1	1020	2
		660	1	1054	2
Myrcene		860	1	1080	3
330	5	910	1	1115	3
403	1	938	1	1155	5
456	1	1017	1	1205	1
525	1	1105	1	1293	2
587	1	1220	1	1311	2
667	2	1302	1	1334	2
735	1	1379	7	{ 1368 }	5
805	1	1446	7	{ 1380 }	2
899	3	1670	15	1397	2
952	1	2915	9	{ 1436 }	15
1003	1	Balata		{ 1456 }	15
1059	2	534	1	1647	15
1103	1	590	1	1668	15
1148	1	910	1	2834	2
1190	1	1002	2	2856	1
1233	1	1027	2	2881	3
1292	8	1101	2	{ 2908 }	4
1330	1	1250	1	{ 2924 }	2
1381	6	1327	1	2964	2
1424	6	1377	1	3048	2
1454	6	1441	1		
1636	15	1670	15		
1675	8	2914	10		
2852	6				
2913	12				
2965	2				
3004	6				
3083	6				

background and the possible coincidence of lines with lines of the solvent, carbon tetrachloride, and carbon bisulfide.

In addition to the frequencies listed for trimethylethylene, we found frequencies of 1214, 1150, and 1097 which are not reported by Bourguet and Piaux. Our material was a commercial sample which we purified by distillation with a Widmer column and treatment with activated charcoal. The relative intensity of the above lines was not altered appreciably by the purification. The fraction used came over between 36.7° and 37.8° and had a refractive index of n_D^{20} 1.3870. These constants

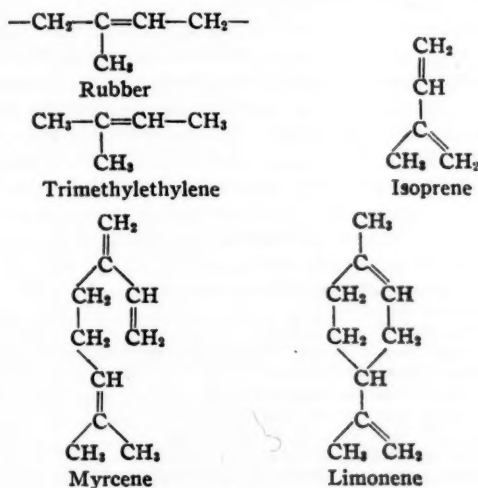
are in good agreement with those of Bourguel and Piaux. It is possible, however, that the above frequencies may be due to traces of allenic impurities in our trimethylethylene, since the strongest lines for methyl-, propyl-, and butyllallene correspond rather closely to the above frequencies.

The generally accepted structural formulas are as follows.¹²

Balata is regarded as a *trans* form of the chain of which rubber is a *cis* form.

In comparing these structures, it will be noted that the double bond in trimethylethylene connects the same general structure as in rubber and balata. There is also a bond of this type in myrcene and likewise in the ring of limonene. The Raman frequency for this linkage for trimethylethylene is 1679 cm^{-1} as compared to 1670 for rubber, 1670 for balata, 1675 for myrcene, and 1668 for limonene. The differences are scarcely larger than experimental errors but nevertheless the value for trimethylethylene appears to be somewhat larger than that for the others. Everything considered, this frequency is remarkably constant. The correspondence between the spectrum of rubber and that of trimethylethylene is not nearly as close as that shown by Signer and Weiler to exist between ethylbenzene and polysterol.

The double bonds in isoprene have a single Raman frequency of 1640 cm^{-1} ,



a value distinctly lower than that for the bonds of the trimethylethylene type. Myrcene has two double bonds similar to the isoprene bonds, in fact a myrcene molecule can be regarded as an isoprene unit joined to a trimethylethylene unit. The external double bond of limonene is also similar to an isoprene bond. Hence we find in the Raman spectrum of myrcene a line of frequency 1636 cm^{-1} of about twice the intensity of the 1675 frequency. Limonene shows lines of frequencies 1647 and 1668 of equal intensity.

The frequencies for myrcene are comprised almost entirely of frequencies of either isoprene or trimethylethylene.

If a rubber molecule consists of long chains of the structural unit with an isoprene group at the end of the chain,¹³ we might expect the Raman spectrum to show the double bond line as a doublet similar to that for myrcene but with the 1640 cm^{-1} component of a small relative intensity depending upon the length of the chains.

The fact that the 1640 cm^{-1} line does not appear may be taken as evidence that the chains are so long that the isoprene group cannot be detected by this method. Our experiments indicate that 5% of isoprene can be detected in trimethylethylene but 1% cannot be.

Although the double bond frequency for balata is the same as that for rubber, the spectra of the two materials appear to be somewhat different. In general, *cis* and *trans* compounds show differences in their Raman spectra⁵ (p. 239), so that the evidence can be looked upon as supporting this relationship between rubber and balata.

We hope to secure a Raman spectrum for vulcanized rubber, using diffusion rubber vulcanized by the Peachey process, and also to study some other rubber derivatives by this method. Results here would open a field of study in which very little indeed is known of the primary chemical linkages.

Abstract

A Raman line spectrum has been secured for rubber and balata by using clear gels of the purified hydrocarbons. It was not found possible to eliminate the background entirely. The most intense frequency for both rubber and balata is the same, 1670 cm^{-1} , ascribed to the double bond.

Comparison of the frequencies for rubber and balata with those of trimethylethylene, myrcene, isoprene, and limonene shows that the primary linkages in rubber are very similar to those in trimethylethylene, thus supporting the view that the rubber molecule consists of a long chain of isopentene units. Differences in the spectra require an explanation, however. The spectrum of balata shows differences from that of rubber such as might be expected from a *cis-trans* relationship.

The spectrum of myrcene is largely a superposition of the isoprene and trimethylethylene spectra.

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Corrosive Action of Sulfur against Metallic Copper during Vulcanization

Shozo Satake

FURUKAWA ELECTROTECHNICAL WORKS, YOKOHAMA

Introduction

The use of copper wire electroplated with tin for insulated electric wires was originated by Siemens eighty-five years ago (through Saito, *J. Soc. Chem. Ind. Japan*, 18, 248 (1915)), and its merits lie in the fact that it prevents a lowering of the electrical conductivity and mechanical strength from corrosion of copper by the sulfur in the rubber, and also prevents the rubber from deteriorating abnormally fast by contact with the copper. The manufacture of rubber for coating wire has improved rapidly since the appearance of organic accelerators and combined accelerating and vulcanizing agents, such as the polynitrobenzenes and benzoyl peroxide of Ostromislensky, the selenium of Boggs and tetramethylthiuram tetrasulfide and tetramethylthiuram disulfide.

Recently, it was reported (*India Rubber World*, 87, 38 (1933)) that rubber compounded with 2 per cent of 1,3,5-trinitrobenzene as vulcanizer does not corrode wire conductors and does not deteriorate abnormally fast when the rubber mixture is covered directly on the wire and vulcanized. The prediction was also made that tin-coated copper wire will disappear entirely from the cable world. As a matter of fact, marine cables have for a long time been covered with an insulator consisting chiefly of gutta-percha or balata hydrocarbon, in direct contact with the copper conductor, and have given good service. The para-gutta insulation of marine cables, recently developed by the Western Electric Company, U. S. A., is composed partly of rubber, with no tin coating on the copper conductor. Nevertheless, the principal factor which decides the "electrical life" of rubber submerged in water is, according to Curtis (*J. Res. Natl. Bur. Standards*, 5, 539 (1930)) the deterioration of the rubber by copper salts, and Asano (*J. Soc. Chem. Ind. Japan*, 24, 336 (1921)) reported that smoked sheet became so sticky that it required considerable strength to separate after it had been held between two copper plates for six months.

The status of the electric insulating wire industry today is such that a thorough investigation of the tin coating of copper wire and the methods of tin coating in connection with the deterioration of rubber by the copper wire is desirable. The investigation described in the present paper was carried on with this object, and it deals with experiments on the corrosion of metallic copper by sulfur during vulcanization, and shows the formation of copper sulfides as corrosion products.

Experimental

Method of Testing the Corrosion.—A mold (diameter 5.64 cm., area 25.0 sq. cm. and thickness 4 mm.), having 16 round holes, was placed on an aluminum plate, the holes were filled with rubber, and covered with an electrolytic copper plate (1 mm. thick, diameter 6.3 cm.), from which adhering fats or oils, and copper

oxide had been previously removed. The assembly was then weighed, after which the copper was covered with another aluminum plate, and the rubber samples vulcanized. The corroded copper was washed with chloroform, then with 5 per cent aqueous sodium cyanate to remove copper sulfide, finally with water, was wiped

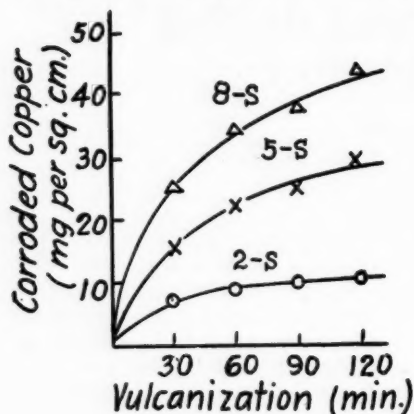


Figure 1

-△- 8 parts of S ($n = 0.42$)
 -X- 5 parts of S ($n = 0.42$)
 -O- 2 parts of S ($n = 0.40$)

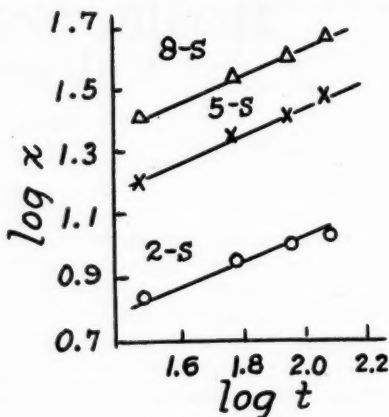


Figure 2

with cloth, and weighed. The corrosion was calculated in milligrams per sq. cm., taking the average of ten test pieces.

Experiment 1. The Relation between the Amounts of Compounded Sulfur and the Corrosion.—Mixtures of 100 parts of smoked sheet (F. A. Q.) with 2, 5, and 8 parts

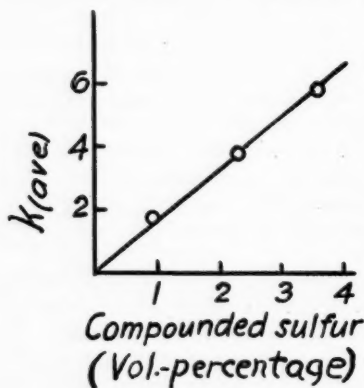


Figure 3

-O- Diphenylguanidine 0.0
 -X- Diphenylguanidine 0.5
 -△- Diphenylguanidine 1.5

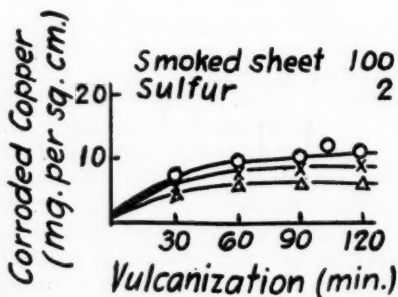


Figure 4

of sulfur were vulcanized at 140° C. for 30, 60, 90, and 120 minutes with the copper plates. The relation of the time of vulcanization and the amount of corroded copper with three rubber samples containing different proportions of sulfur is shown in Fig. 1.

The corrosion during the initial period shows a parabolic relation with increase in time. Let x be the amount of corroded copper (mg. per sq. cm.), and t the time of vulcanization (in minutes), then $x = Kt^n$. The relation of $\log x$ and $\log t$, as indicated in Fig. 2, can be expressed by a straight line, and the value of n is found to be 0.40–0.42. The value of K is calculated from these values as follows:

Rubber 100, Sulfur 2 $n = 0.40$		Rubber 100, Sulfur 5 $n = 0.42$		Rubber 100, Sulfur 8 $n = 0.42$	
t	K	t	K	t	K
30	1.713	30	3.811	30	5.992
60	1.748	60	3.977	60	6.130
90	1.664	90	3.831	90	5.784
120	...	120	3.909	120	5.759
Average 1.708		Average 3.882		Average 5.917	

The amount of sulfur (volume-percentage) in these three samples is calculated on the basis that the specific volume of rubber is 1.08 and that of sulfur is 0.50.

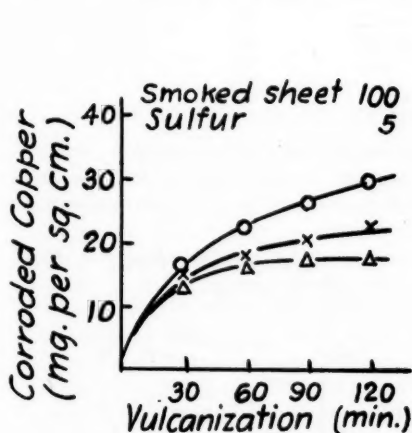


Figure 5

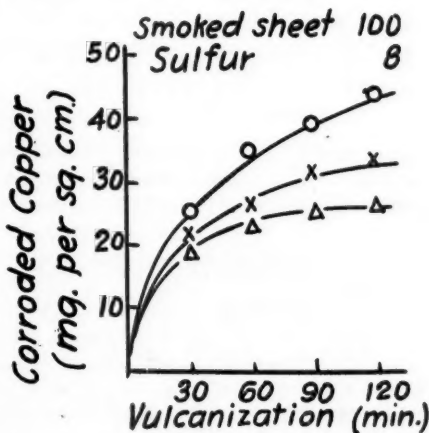


Figure 6

-O- Diphenylguanidine 0.0
 -X- Diphenylguanidine 0.5
 -Δ- Diphenylguanidine 1.5

The average values of K , as shown in Fig. 3, are directly proportional to the total sulfur.

Experiment 2. The Relation of the Proportion of Vulcanization Accelerator and the Corrosion.—To three samples of the same composition as in the preceding experiment, diphenylguanidine was added in three percentages, viz., 0.5 and 1.5 parts per 100 parts rubber, and the corrosion was determined as before. Figures 4, 5, and 6 show the relation between the proportion of accelerator and the extent of corrosion of the copper as affected by the time when 2, 5, and 8 parts of sulfur are used. It is clear that the corrosion tends to decrease with increase in the time of vulcanization.

Figures 7 and 8 show the relation between $\log x$ and $\log t$ in three rubber samples containing different proportions of sulfur, and 0.5 and 1.5 parts of diphenylguanidine per 100 parts rubber. These are also straight lines, but an increase in the accelerator caused a decrease in the value of n in all cases. Calculation of the value of K from these results showed that K increased with increase in accelerator. The

proportion of sulfur (volume-percentage) calculated on a basis of the specific volume of diphenylguanidine as 0.91, as in the preceding experiment, and Fig. 9 shows that K and the sulfur are directly proportional.

Rubber 100
D. P. G. 0.5
Sulfur 2
 $n = 0.30$

t	K
30	2.169
60	2.193
90	2.150
120	...

Average 2.171

Rubber 100
D. P. G. 1.5
Sulfur 2
 $n = 0.18$

t	K
30	2.619
60	2.631
90	2.589
120	...

Average 2.613

Rubber 100
D. P. G. 0.5
Sulfur 5
 $n = 0.30$

t	K
30	5.321
60	5.087
90	5.146
120	5.192

Average 5.187

Rubber 100
D. P. G. 1.5
Sulfur 5
 $n = 0.22$

t	K
30	6.170
60	6.465
90	6.349
120	...

Average 6.328

Rubber 100
D. P. G. 0.5
Sulfur 8
 $n = 0.32$

t	K
30	7.139
60	6.995
90	7.295
120	7.129

Average 7.140

Rubber 100
D. P. G. 1.5
Sulfur 8
 $n = 0.22$

t	K
30	9.268
60	9.506
90	9.268
120	...

Average 9.348

Experiment 3. The Relation between the Temperature of Vulcanization and the Corrosion.—The relation between the temperature of vulcanization and the corrosion was studied with a rubber-sulfur (100:5) mixture with copper plate and

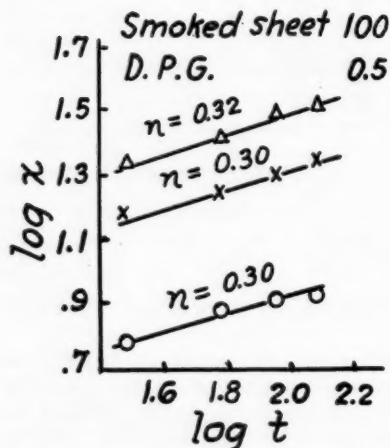


Figure 7

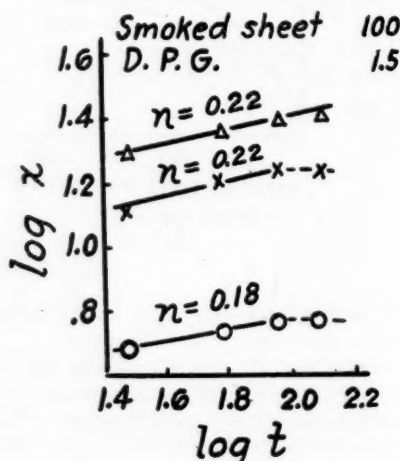


Figure 8

-Δ- Sulfur 8 parts
-X- Sulfur 5 parts
-O- Sulfur 2 parts

vulcanized at 160°, 140° (from the data of Experiment 1), and 120° C. The results are shown in Figs. 10 and 11, which show that $\log x$ and $\log t$ are directly proportional. Figure 11 also shows that n decreases with increase in the temperature of vulcanization.

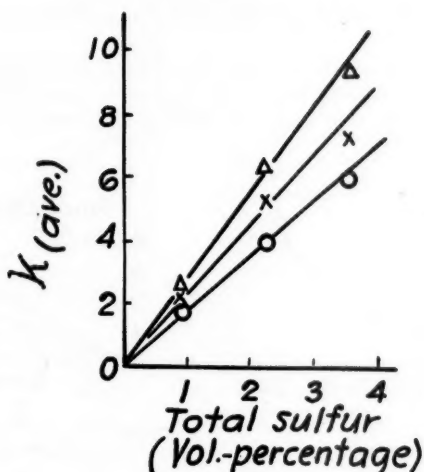


Figure 9

-Δ- Diphenylguanidine 1.5 parts
 -X- Diphenylguanidine 0.5 part
 -O- Diphenylguanidine 0.0 part

The value of K is calculated from these values, and Fig. 12 shows that K increases with an increase in the temperature of vulcanization.

Experiments 1, 2, and 3 show that an increase in the proportion of accelerator and the temperature decreased n and increased K . Since an accelerator and an increase in the temperature of vulcanization caused a change in the velocity of the vulcanization reaction, the relation between K and n and the velocity of vulcanization was studied by the following method. To determine the velocity of vulcanization of the mixtures used in the preceding experiments, another set of samples was prepared with the same mixtures and the same mold, and was vulcanized in a press with two aluminum plates as in the corrosion test. The free sulfur after vulcanization

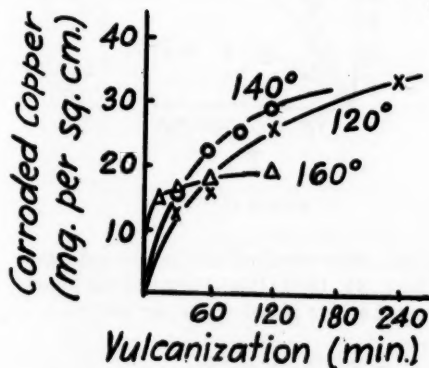


Figure 10

-O- 140° C. ($n = 0.42$)
 -X- 120° C. ($n = 0.50$)
 -Δ- 160° C. ($n = 0.14$)

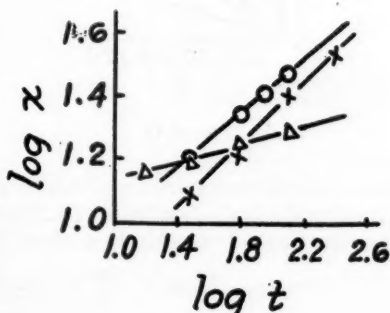


Figure 11

was determined, and the combined sulfur and the coefficient of vulcanization were calculated.

Figures 13, 14, and 15 show the relation between the vulcanization coefficients (V) and the times of vulcanization (t) for samples containing three different proportions of sulfur with 0, 0.5, and 1.5 parts of diphenylguanidine per 100 parts

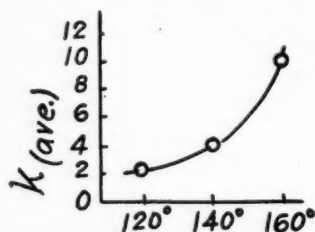


Figure 12

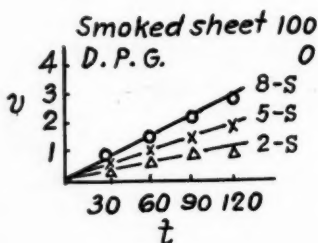


Figure 13

rubber. Figure 16 shows the relation between the vulcanization coefficients and the times of vulcanization of rubber-sulfur (100:5) mixtures vulcanized at 160°, 140°, and 120° C.

Toyabe (*J. Soc. Chem. Ind. Japan*, 33, 316 (1930)) has concluded that the velocity of vulcanization cannot be expressed by a straight line, but can be represented by a curve which is nearly a straight line. It is generally agreed, how-

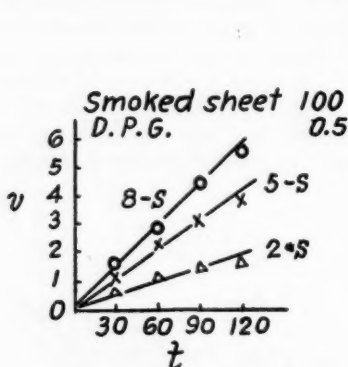


Figure 14

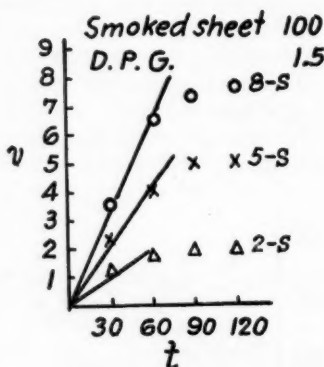


Figure 15

ever, that the vulcanization of rubber is a first order reaction and can be expressed by a straight line. Nordlander (*J. Phys. Chem.*, 34, 1869 (1930)) derived the following equation for vulcanization when the total sulfur is below 10 per cent:

$$\frac{dV}{dt} = k. \quad \frac{dV}{dt} = k'[S_\mu]. \quad k' = [S]_0[K_s + K_a[A]]$$

where V is "vulcanization coefficient" in t hours, k and k' are the velocity constants of vulcanization, $[S_\mu]$ is the concentration of S_μ in melted sulfur, which increases

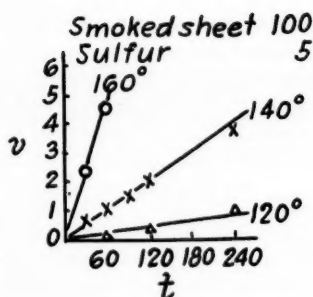


Figure 16

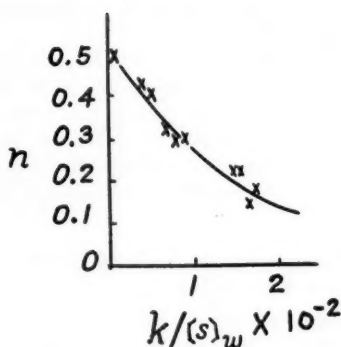


Figure 17

with an increase in temperature, $[S]_w$ is the percentage (by weight) of total sulfur, K is the vulcanization constant of the rubber hydrocarbon and substances naturally in the rubber, $[A]$ is the percentage (by weight) of the vulcanization accelerator, and K_a is the vulcanization constant of the accelerator.

In the equation above let the velocity of the vulcanization reaction be expressed as a straight line; then k is estimated from the slopes in Figs. 14, 15, and 16, $k/[S]_w$ is calculated from the equation above, and its relation with n is shown in Fig. 17.

Here $k/[S]_w$ shows the velocity constant of vulcanization which is related to the temperature of vulcanization and the type and proportion of accelerator. Figure 17 shows that n decreased regularly with an increase in $k/[S]_w$. Since K is directly related to the total sulfur $[S]_w$ (volume-percentage) (see Fig. 19), the relation of $K/[S]_w$ and $k/[S]_w$ is indicated in Fig. 18, in which $K/[S]_w$ increased with an increase in the velocity constant of vulcanization. This increase was not so great

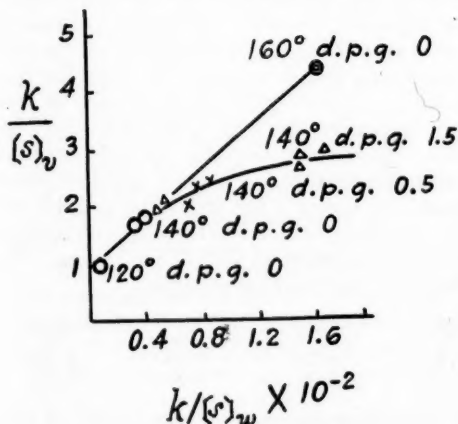


Figure 18

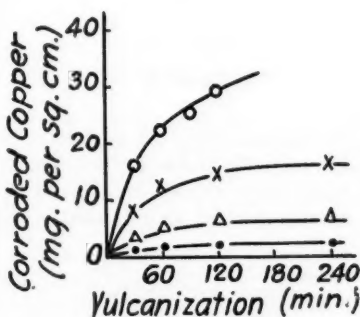


Figure 19

- Free Sulfur 4.76% (cured 2 hrs.)
- x- Free Sulfur 2.84% (cured 2 hrs.)
- △- Free Sulfur 1.01% (cured 4 hrs.)
- Free Sulfur 0.30% (cured 6 hrs.)

with the accelerator, whereas an increase in the temperature of vulcanization had a marked influence.

Experiment 4. The Relation between the Combined (Acetone-Insoluble) Sulfur and the Corrosion.—Nine mixtures used in the corrosion tests of Experiments 1 and 2 were placed in the same mold and vulcanized at 140° C. for 2 hours by pressing both sides with aluminum plates; the free sulfur was removed by extraction with acetone and the corrosion of the copper estimated by the combined sulfur of the samples. The result is indicated in the following table.

Rubber	Sulfur	Diphenylguanidine	Percentage Combined Sulfur	Weight of Rubber (G.)	Weight of Corroded Cu (Mg. per Sq. Cm.)
100	2	0.0	1.00	8.84	0.036
100	5	0.0	1.92	8.46	0.060
100	8	0.0	2.68	8.90	0.080
100	2	0.5	1.75	9.09	0.035
100	5	0.5	3.69	9.03	0.047
100	8	0.5	5.10	9.16	0.067
100	2	1.5	1.91	9.02	0.018
100	5	1.5	4.65	9.48	0.020
100	8	1.5	7.21	9.71	0.045

It is clear from this table that the corrosion caused by combined sulfur is very slight (the amount of corroded copper is an average of duplicate tests).

Using the same procedure, a rubber-S (100:5) mixture was vulcanized in a press at 140° C. for 2, 4, and 6 hours; then the corrosion was determined at 140° C.

in order to ascertain the relation between the corrosion and the free sulfur content. Figure 19 shows clearly that the corrosion of the copper plate is due to the action of free sulfur. (A case of undervulcanized sample which contained 4.76 per cent of free sulfur was taken from the data of Experiment 1.)

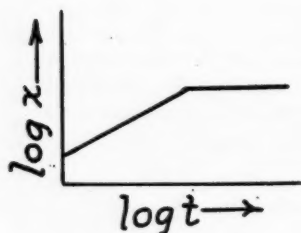


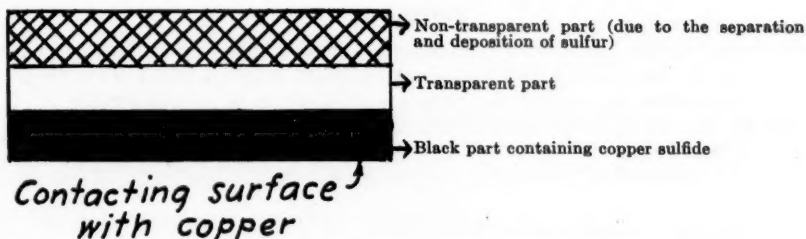
Figure 20

The action of free sulfur on metallic copper is very marked, and the state of corrosion revealed that the sulfur in contact with the copper reacted first (part of the sulfur seemed to combine with the rubber), and it appears that when the concentration of free sulfur at the surface of contact decreases, the free sulfur away from the surface of contact migrates by diffusion and reacts with the copper. Accordingly, the further

its distance from the surface of contact, the higher is the free sulfur contact and the higher is the rate of vulcanization. An example of this is the corrosion brought about by a rubber-sulfur (100:8) mixture vulcanized at 140° C. for 2 hours. The sample showed, as indicated in the diagram, the following analysis.

	Free S (%)	Combined S (%)	Total S (%)	Compounded S (%)
Non-transparent part	3.53	2.51	6.04	7.41
Transparent part	1.17	2.07	3.24	7.41

The concentration of free sulfur in the rubber decreased as part combined with the rubber, and finally became zero. Since the corrosion of copper by combined sulfur is slight, the relation of $\log x$ and $\log t$ is that shown in Fig. 20. In Fig. 8 the parts of the curves shown by dotted line contained no free sulfur, as was confirmed by analysis.



Experiment 5. Chemical Constitution of the Copper Sulfide Produced by Corrosion.—The corrosion products (containing copper sulfide) formed at the surface of contact between the copper plates and nine samples of rubber in the 120 minutes' corrosion tests of Experiments 1 and 2 were collected separately, placed in a large quantity of xylene, heated at 130°C . to dissolve the rubber, the xylene was removed, and the precipitate of copper sulfide was washed with naphtha several times, placed on the filter, washed with warm naphtha, and dried. A weighed quantity of the product was dissolved in a small quantity of concentrated nitric acid, and evaporated to dryness after addition of a small quantity of concentrated sulfuric acid. The quantity of copper was estimated by electrolysis of the copper sulfate, and the constitution of the copper sulfide was studied from the results. The results indicate that the chemical constitution of the copper sulfide was nearly the same in all cases, and had no relation to the proportion of total sulfur or accelerator. The average copper content of the copper sulfide was 76.40 per cent (maximum 76.80, minimum 76.12). These data indicate that the copper sulfide produced by the corrosion was not cuprous sulfide, or cupric sulfide, for the average copper content corresponded to the formula, $5\text{Cu}_2\text{S} \cdot 3\text{CuS}$ (76.30 per cent Cu); the sulfide containing the maximum copper was close to the formula, $2\text{Cu}_2\text{S} \cdot \text{CuS}$ (76.78 per cent Cu), and that of the minimum copper content was $3\text{Cu}_2\text{S} \cdot 2\text{CuS}$ (76.03 per cent Cu). It has already been reported by Hayward (*Chem. Met. Eng.*, 18, 650 (1918)) that the corrosion products of copper by boiling sulfur for 5 minutes to 5 hours showed nearly the same copper content; the formula was $5\text{Cu}_2\text{S} \cdot 2\text{CuS}$ (77.38 per cent copper). It is interesting to note that the results of the present author and those of Hayward are nearly the same, and it is probable that the same results would have been obtained if the corrosion test by the present author had been continued longer than 2 hours. The copper sulfide thus obtained should be regarded as a mixture of Cu_2S and CuS , in the ratio of 5:3, rather than a molecular compound of Cu_2S and CuS .

1. The corrosion of metallic copper by sulfur during vulcanization was studied by vulcanizing rubber mixtures in contact with copper plates. It was found that the state of corrosion can be expressed in many cases by the equation: $x = Kt^n$, where x is the amount of corrosion in t hours, and K and n are constants which depend on the experimental conditions. That n is inversely proportional to the velocity constant of vulcanization, which is related only to the temperature of vulcanization and to the type and proportion of accelerator was proved by estimating the velocity of vulcanization of the same rubber mixtures and under the same conditions of vulcanization as in the corrosion tests. That K is directly proportional to the total sulfur (volume-percentage) is confirmed, and the relation between K and the velocity constant of vulcanization was also studied.

2. The corrosive action of combined sulfur (acetone-insol. sulfur) in vulcanized rubber is slight, and it was proved that the corrosion of metallic copper during vulcanization is mainly caused by free sulfur. A study of the chemical constitution

Summary

of the copper sulfide produced by the corrosion showed that it is a mixture of Cu_2S and CuS in the ratio of 5:3, and that its constitution is independent of the proportion of accelerator or even of the presence or absence of an accelerator.

Thanks are due to Furukawa Electro-Industrial Company for permission to publish this article.

Fundamental Studies on the Attributes of Organic Accelerators

XI. Peculiarity of Some Accelerators toward Rubber Sols

Keichi Shimada

KIRYU HIGHER TECHNICAL SCHOOL

In so far as the author's new classification of organic accelerators into three groups, A, B, and C, is concerned, the characteristics of accelerators belonging to Group C have already been discussed, and it is not necessary at this time to deal with those belonging to Group A, as they have no special characteristics from the colloid chemical standpoint. Group C accelerators are merely substances to be distinguished from accelerators in Group B, which disaggregate rubber sols (*J. Soc. Chem. Ind. Japan*, 35, 1206 (1932)). To confirm this assumption experimentally, the relation between the characteristics of Group B accelerators and the amounts to be added to rubber sols was studied.

Experimental

According to the author's classification, there are twelve commercial organic accelerators which belong to Group B, viz., hexamethylenetetramine, ethylidene-aniline, acetaldehyde-aniline, heptaldehyde-aniline, triethyltrimethylenetriamine, diphenylguanidine, phenyl-*o*-tolylguanidine, di-*o*-tolylguanidine, *o*-tolylbiguanide, piperidinepentamethylene dithiocarbamate and cyclohexylethylamine dithiocarbamate.

It has already been pointed out by the author that Group B accelerators have the characteristic of causing a marked depression in the viscosity of rubber sols in a very short time, with a subsequent slight change. In the preceding report, the final measurements of the viscosity were made five hours after the addition of accelerator. In the present experiments, the changes in viscosity of rubber solutions in benzene with Group B accelerators were measured after 24 hours' standing. The experimental method was the same as described in the Fourth Report (*J. Soc. Chem. Ind. Japan*, 36, 202 (1933)). Table I shows the results. The preceding experiments on the viscosities of rubber sols fifteen minutes and five hours after the addition of accelerators are also included for comparison. The viscosities are expressed in time (seconds required for running out at 23°). To study the relation between the behavior of Group B accelerators and the proportions added, as tested with Group C accelerators (*J. Soc. Chem. Ind. Japan*, 36, 203 (1933)), the effect of adding various amounts of diphenylguanidine and di-*o*-tolylguanidine on the viscosity of the rubber solutions in benzene was investigated. The additions were varied from 0.002 gram to 0.01 gram per 10 cc. of rubber sol (0.3 gram in 100 cc. benzene). It has already been stated that Group B accelerators lower the viscosity of rubber sols in a very short time and the effect of time thereafter is unimportant. Nevertheless, the author took the precaution to measure the viscosities exactly fifteen minutes after the addition of the accelerator. Ten times the weight of each accelerator to

be added was added to 10 cc. of rubber-benzene sol, and 1 cc. was pipetted out into a rubber sol, which was placed in an Ostwald viscometer and kept at $22 \pm 0.03^\circ \text{C}$. The method of measurement was the same as described in the Fourth Report. Tables II and III show the results; the viscosities of the rubber sols before the addition of accelerators are expressed as the times in seconds required by the 10 cc. of rubber sol plus 1 cc. benzene.

TABLE I
EFFECT OF TIME ON THE VISCOSITIES OF RUBBER SOLS WITH GROUP B ACCELERATORS
(Concn. of Rubber: 0.04 Gram per 100 Cc.; Accelerator Added: 0.004 Gram)

Accelerator	Viscosity (Sec.)— Time of Standing (Hrs.)			
	Before	1/4	5	24
Hexamethylenetetramine	156.0	152.1	151.3	151.0
Ethylidene-aniline	156.0	152.0	151.2	149.4
Acetaldehyde-aniline	154.2	141.6	140.9	140.8
Heptaldehyde-aniline	150.0	140.6	139.3	139.0
Triethyltrimethylenetriamine	150.0	141.5	140.3	140.3
Diphenylguanidine	156.4	147.4	145.6	144.2
Di- <i>o</i> -tolylguanidine	156.4	144.9	143.7	142.5
Phenyl- <i>o</i> -tolylguanidine	159.3	149.0	147.4	147.0
Triphenylguanidine	157.4	155.7	155.3	153.5
<i>o</i> -Tolylbiguanide	159.0	151.2	150.2	149.2
Piperidinepentamethylene dithiocarbamate	156.4	146.4	145.6	142.0
Cyclohexylethylamine dithiocarbamate	156.4	145.8	144.3	143.6

The relation between the weights of accelerator added and the lowering of the viscosity of the rubber sols is also shown in Figs. 1 and 2.

Discussion of the Results

The results in Table I show that the effect of time on the lowering of the viscosities of rubber sols by the addition of Group B accelerators was very slight, and there was practically no difference in the viscosities of those which stood for five hours and for twenty-four hours. The peculiar action of these Group B accelera-

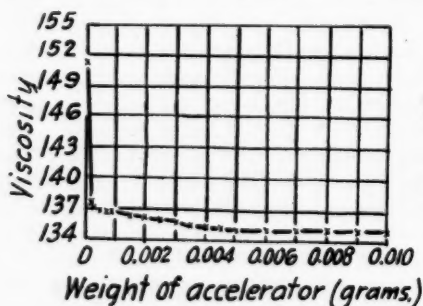


Figure 1—Diphenylguanidine

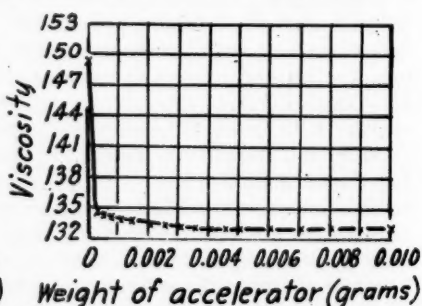


Figure 2—Di-*o*-tolylguanidine

tors on rubber sols thus appeared within 30 minutes, and this fact is an important proof that the lowering of the viscosity of dilute rubber solutions by the addition of Group B accelerators is not caused by a depolymerization of the rubber molecules as in the case of Group C accelerators. A study of the results in Tables II and III shows that there was practically no difference in the lowering of the vis-

cosity of those containing either small or large proportions of Group B accelerators in the rubber sol.

Thus the lowering of the viscosity of the rubber sol containing only 0.67 per cent of diphenylguanidine (based on the solid rubber) was 9.18 per cent, while an increase in the amount of accelerator to 26.67 per cent was only 10.77 per cent. This is another way in which Group B accelerators differ from those of Group C. In general, the addition of 0.004–0.005 gram of Group B accelerators to a rubber sol with a concentration of 0.3 gram per 100 cc. gave the maximum change in viscosity, and there was practically no further change in viscosity by adding more than this proportion. Were the proportion of accelerator increased enormously, there might be some change, but the scope of the present experiments was limited to not over 0.01 gram, as the solubility of the accelerators in benzene had to be taken into account.

TABLE II
DIPHENYLGUANIDINE

Weight of Accelerator	Viscosity		Weight of Accelerator	Viscosity	
	Before Addn.	After Addn.		Before Addn.	After Addn.
0.0002	151.4	137.5	0.0030	151.3	135.8
0.0003	151.2	137.1	0.0035	151.5	135.4
0.0005	151.5	136.9	0.0040	151.4	135.2
0.0007	151.5	136.8	0.0045	151.4	135.2
0.0009	151.4	136.7	0.0050	151.2	135.1
0.0010	151.3	136.6	0.0060	151.1	135.1
0.0015	151.5	136.4	0.0070	151.3	135.0
0.0020	151.3	136.2	0.0080	151.1	135.1
0.0025	151.1	136.0	0.0100	151.3	135.1

TABLE III
DI-*o*-TOLYLGUANIDINE

Weight of Accelerator	Viscosity		Weight of Accelerator	Viscosity	
	Before Addn.	After Addn.		Before Addn.	After Addn.
0.0002	149.8	139.4	0.0035	149.3	133.2
0.0003	149.6	134.7	0.0040	149.2	133.0
0.0005	149.7	134.4	0.0045	149.5	133.0
0.0008	149.8	134.2	0.0050	149.3	133.0
0.0010	149.5	134.0	0.0060	149.1	133.1
0.0015	149.4	133.8	0.0070	149.2	133.0
0.0020	149.6	133.5	0.0080	149.0	133.1
0.0025	149.3	133.4	0.0090	149.2	133.0
0.0030	149.6	133.3	0.0100	149.1	133.0

The difference in the effects on the viscosity arising from the fact that the accelerators are liquids in some cases and solids in others must also be taken into account.

In short, the results show that there are approximate limits to the proportions of Group B accelerators to be added in order to develop the maximum effects, above which limits there are no corresponding increases in the effects. This fact is a proof of the author's theory that accelerators belonging to Group B have no ability to depolymerize the rubber molecules.

The author proposed a hypothesis in the Ninth Report of this series (*J. Soc. Chem. Ind. Japan*, 36, 1121 (1933)) on the structure of rubber solution that rubber molecules in dilute solutions exist as separate individuals, yet there remains a micelle structure, and the Group B accelerators have the property of separating these remaining micelles.

There is reason to believe that dilute rubber solutions contain to a limited extent a micellar structure, since the addition of a very small proportion of Group B accelerators causes a considerable lowering of the viscosity in a short time, with no change above this limit. That the author's theory of the cause of the lowering of viscosity of dilute rubber solutions by the addition of Group B accelerators disaggregation of the rubber is supported by this important fact.

Summary

1. The changes in the viscosity of rubber sols by the addition of Group B accelerators is a result of depolymerization, since the time effect in the changes in the viscosities of benzene solutions of rubber by the addition of the accelerators are very slight.
2. There are approximate limits to the proportions of Group B accelerators where they develop their maximum effects on rubber sols, and above which the effects are not noticeably greater. This supports the author's theory that Group B accelerators do not cause depolymerization of rubber.
3. An experimental proof is furnished in support of the author's theory that Group B accelerators bring about disaggregation of rubber.

XIV. Supplement to "Observations on the Behavior of Organic Accelerators toward Rubber Solutions"

The author has already proposed to divide organic accelerators into three groups, designated A, B, and C, and based on experiments on the effects of thirty commercial accelerators on the viscosities of rubber sols (*J. Soc. Chem. Ind. Japan*, **35**, 1188 (1932)). Group A had no effect, Group B caused disaggregation, and Group C caused depolymerization of the rubber. After a careful study of the relation between the concentrations of rubber and the surface tensions of the solutions, a hypothesis was advanced to account for the structure of dilute rubber solutions (*J. Soc. Chem. Ind., Japan*, **36**, 1117 (1933)), and it was necessary to make certain corrections of the mechanism of the action of certain accelerators.

A Supplementary View of the Action of Heat on Rubber Solutions

In the studies of the action of heat on rubber solutions, the author considered that the irreversible change in viscosity brought about by heating is attributable to a division of the rubber molecules, *i. e.*, a depolymerization by chemical means (*J. Soc. Rubber Ind. Japan*, **3**, 431 (1931)).

The previous study (*loc. cit.*) on the relation between the concentration of rubber and the surface tension of the solution indicated that rubber molecules in dilute solutions exist chiefly in chain form, with small proportion of colloidal particles in the form of micelles. The higher the concentration, the more micelles are formed.

The question arises whether the micelles are destroyed by heating. Though the author thought that the continuous lowering of the viscosity of a dilute rubber solution by heating is attributable to a depolymerization of the rubber molecules, as the change of viscosity is irreversible, this assumption was based on the further belief that the solution is molecular, as considered by Staudinger. Suppose now that a dilute solution of rubber still has a partially micellar structure, it is right to consider that the micelles are destroyed by heating, which results in a lowering of the viscosity.

The action of heat on a dilute solution of rubber is best explained as follows. When a dilute solution of rubber is heated, the change observable is a result of the destruction of the remaining micelles and the formation of a molecular solution which consists entirely of chain molecules; the second process is a continuous and slow depolymerization of these independent molecules. Accordingly, on heating there must be a lowering of the viscosity as a result of disaggregation, during the initial period, in the viscosity-time curve.

The Effect of Group C Accelerators on Rubber Solutions

The viscosity-time curves of rubber solutions containing thirty commercial organic accelerators were determined, and it was found that there are three distinct types of curves, *viz.*, groups A, B, and C (*loc. cit.*).

Since the lowering of the viscosity by addition of Group C accelerators is closely similar to the change in the viscosity-time curves representing the heating of dilute solutions of rubber, Group C accelerators supposedly cause a depolymerization of the rubber. Though this view is not considered to be incorrect, since heat causes disaggregation and depolymerization of a dilute rubber solution, the action of Group C accelerators must also bring about a destruction of the remaining micelles in the rubber solution, with subsequent depolymerization. It may therefore be rightfully considered that the effect of Group B accelerators on dilute rubber solutions is a disaggregation, while that of Group C accelerators is a disaggregation and depolymerization.

Views as to the action of Group C accelerators must therefore be corrected, and further studies will be carried on from this point of view.

Summary

Experiments lead to a revision of former views regarding the action of heat and of Group C accelerators on rubber solutions. The changes in the viscosities of dilute rubber solutions by heating or by the addition of Group C accelerators are attributed to a destruction of the remaining micelles, *i. e.*, a disaggregation and subsequent depolymerization of the rubber molecules thus formed and those already present.

The Oil Resistance of Rubber

II. Molecular Polarization and Dipole Moment of Purified Natural Rubber

Shû Kambara

LABORATORY OF RUBBER CHEMISTRY AND TECHNOLOGY, TOKYO UNIVERSITY COLLEGE OF TECHNOLOGY, TOKYO, JAPAN

1. Introduction

Natural rubber is assumed to be a non-polar substance, considering the fact that rubber is greatly swollen by non-polar solvents, and that isoprene has a very small dipole moment (cf. Smyth and Walls, *J. Chem. Physics*, 1, 200 (1933); Farmer and Warren, *J. Chem. Soc.*, 1933, 1297). Few works, however, have been published on the molecular polarization of rubber. Ostwald and Riedel studied the polarization of masticated crude rubber, and obtained comparatively large values (cf. *Kolloidchem. Z.*, 70, 75 (1935)). The present author considers that to improve the oil resistance of rubber goods, research on the molecular polarization of rubber and its derivatives is very important. This paper is concerned with the problem whether the high molecular polarization, as determined by Ostwald and Riedel, is attributable to impurities in the rubber hydrocarbon, which are very difficult to remove, to the molecular arrangement of the rubber hydrocarbon, or to the oxidation of the rubber. For this reason, purified rubber obtained by the method of Pummerer was used in all the experiments described in this paper.

2. Experimental

The density, dielectric constant, and refractive index of purified rubber solutions were determined by ordinary methods. The dielectric constant was measured by means of the zero beat method, using a 500 kilocycle heterodyne oscillator, as shown in Fig. 1. From the data obtained at various concentrations, the molecular polarizations were calculated by Debye's formula. To represent the concentration by the mol fraction, and to calculate the molecular polarization, the molecular weight of rubber should be known. As this value has never been established, it was assumed that the mean molecular weight of rubber is eight times that of isoprene, or that the rubber molecule in dilute solution behaves statistically in an electric field as a group consisting of eight isoprenes. This assumption is based on x-ray studies by Hauser and Mark (*Kolloidchem. Beihefte*, 22, 63; 23, 64 (1926)) and cryoscopic studies by Pummerer (*Ber.*, 60, 2167 (1927)).

Rubber was purified as described by Pummerer (*Ber.*, 61, 1583 (1928)). The purified rubber was a pale yellowish elastic mass with 0.11 per cent of ash. The following four solutions were prepared from the purified rubber.

- A. Total rubber-benzene solution.
- B. Gel rubber-benzene solution.
- C. Sol rubber-ether solution.
- D. Sol rubber-benzene solution.

The purified rubber was dissolved in benzene to make about a 3 per cent solution. After shaking one day, the undissolved residue was filtered off on a glass filter. The filtrate was used as a total rubber-benzene solution. The purified rubber was

extracted by ether for 40 hours in a Soxhlet extractor. The residue in the extractor was dried in a stream of carbon dioxide and in a high vacuum, and was then dissolved in benzene. The liquor thus obtained was used as a gel rubber-benzene solution. Ether collected in the bottom flask of the extractor, used to prepare the gel rubber, was regarded as a sol rubber-ether solution. To prepare its benzene

Fig. 1 A—Crystal oscillator

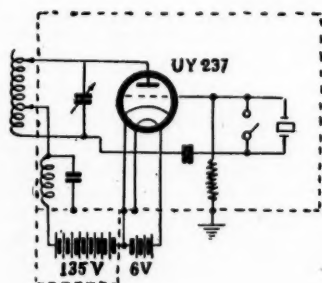


Fig. 1 B—Dinatron oscillator

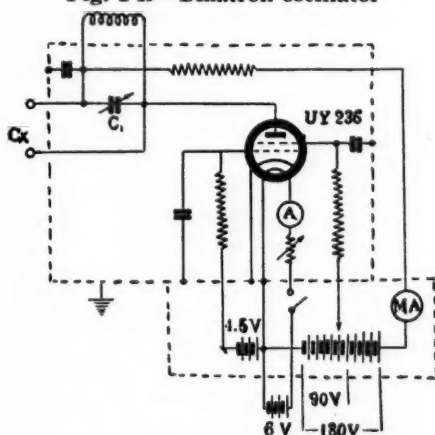
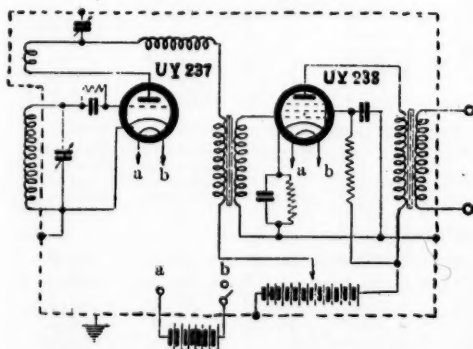


Fig. 1 C—Receiver



solution, the sol rubber-ether solution was dried in a high vacuum. A brownish tacky mass was obtained after complete drying. Because the mass was difficult to dissolve in benzene, its extracted liquor with benzene was used as the sol rubber-benzene solution.

Benzene (Kahlbaum) was refined by drying with P_2O_5 , distilling with metallic sodium, recrystallizing three times, and blowing in oxygen-free, dry CO_2 gas to remove dissolved oxygen in the solvent. Ether (Kahlbaum distilled over sodium) was used after two distillations with metallic sodium.

The concentration of all solutions was calculated from the weights of the dried residue. To dilute the solution, the same solvent was added, and to concentrate it, dry CO_2 gas was blown in. These procedures were performed alternately, and suf-

ficiently not to alter remarkably the state of solute. In the following tables, $P_{1,2}$ is the molecular polarization of the solution, and P_2 is that of rubber. These were calculated as described by C. P. Smyth ("Dielectric Constants and Molecular Structure," p. 28). $P_{E,2}$ (electron polarization of rubber) was calculated from the refractive index, density, and molecular weight of rubber. The refractive index was obtained by extrapolation of the index of the rubber solution in accordance with the volume-per cent concentration. The density is the extrapolated value of that of solution in accordance with the weight-per cent concentration.

TABLE I
A. TOTAL RUBBER-BENZENE SOLUTION

Concentration W%	Mol. Fraction C_1	Density d_{15}^{25}	Dielectric Constant	Refractive Index n_D^{25}	Molecular Polariza- tion of Solution $P_{1,2}$	Molecular Polariza- tion of Rubber P_2	Electron Polariza- tion of Rubber $P_{E,2}$
0.000	0.00000	0.8744	2.288	1.5000	26.81
0.653	0.00094	0.8748	2.292	1.5001	27.01	240.5	175.9
0.972	0.00133	0.8750	2.298	1.5002	27.15	287.5	177.4
1.676	0.00244	0.8755	2.312	1.5004	27.53	321.0	180.0
1.920	0.00280	0.8757	2.316	1.5005	27.64	322.6	176.4
2.691	0.00395	0.8762	2.326	1.5006	27.95	317.2	177.0
3.213	0.00474	0.8765	2.335	1.5008	28.18	316.0	178.5
4.201	0.00625	0.8772	2.349	1.5009	28.59	312.8	176.8

B. GEL RUBBER-BENZENE SOLUTION

Concentration W%	Mol. Fraction C_1	Density d_{15}^{25}	Dielectric Constant	Refractive Index n_D^{25}	Molecular Polariza- tion of Solution $P_{1,2}$	Molecular Polariza- tion of Rubber P_2	Electron Polariza- tion of Rubber $P_{E,2}$
0.000	0.00000	0.8744	2.288	1.5000	26.81
0.480	0.00069	0.8748	2.296	1.5002	27.02	334.1	180.0
1.533	0.00233	0.8761	2.316	1.5008	27.52	347.7	180.1
1.971	0.00287	0.8775	2.328	1.5010	27.76	358.3	171.1
2.548	0.00373	0.8778	2.340	1.5011	28.07	364.4	175.0
3.996	0.00592	0.8790	2.368	1.5014	28.80	363.2	172.7

C. SOL RUBBER-ETHER SOLUTION

Concentration W%	Mol. Fraction C_2	Density d_{15}^{25}	Dielectric Constant	Refractive Index n_D^{25}	Molecular Polariza- tion of Solution $P_{1,2}$	Molecular Polariza- tion of Rubber P_2	Electron Polariza- tion of Rubber $P_{E,2}$
0.000	0.00000	0.7090	4.268	1.3532	54.48
0.417	0.00057	0.7101	4.264	1.3538	54.56	194.8	186.9
1.456	0.00201	0.7123	4.248	1.3550	54.75	191.8	180.8
2.003	0.00278	0.7135	4.244	1.3559	54.89	203.8	185.4
2.184	0.00303	0.7139	4.240	1.3562	54.91	198.7	186.4
3.181	0.00445	0.7164	4.228	1.3580	55.11	196.1	190.9
3.566	0.00501	0.7169	4.222	1.3585	55.21	200.6	190.9
4.311	0.00610	0.7187	4.211	1.3592	55.36	198.6	186.6

D. SOL RUBBER-BENZENE SOLUTION

Concentration W%	Mol. Fraction C_1	Density d_{15}^{25}	Dielectric Constant	Refractive Index n_D^{25}	Molecular Polariza- tion of Solution $P_{1,2}$	Molecular Polariza- tion of Rubber P_2	Electron Polariza- tion of Rubber $P_{E,2}$
0.000	0.00000	0.8744	2.288	1.5000	26.81
0.539	0.00078	0.8745	2.298	1.5002	27.07	368.3	160.7
0.771	0.00111	0.8747	2.300	1.5003	27.15	347.7	187.3
1.185	0.00172	0.8757	2.310	1.5004	27.36	350.3	173.3
1.752	0.00255	0.8759	2.318	1.5006	27.61	341.8	177.4
2.359	0.00345	0.8762	2.324	1.5008	27.87	337.6	178.9
2.715	0.00399	0.8769	2.328	1.5009	27.96	316.2	175.9
3.299	0.00487	0.8773	2.332	1.5011	28.15	302.8	176.7

From the above data, $P_{\infty 2}$ is difficult to obtain, as P_2 does not show a proper relation to C_2 . \bar{P}_2 is a mean value of P_2 , and this is regarded as the mean molecular polarization. The dipole moment is calculated as follows.

$$\mu = 0.0127 \times 10^{-18} \sqrt{(\bar{P}_2 - P_{E,2}) \times T} \text{ e. s. u.}$$

TABLE II

Solute	Solvent	\bar{P}_2	$P_{E,2}$	$\mu \times 10^{18} \text{ e. s. u.}$
Total rubber	Benzene	302.5	177.4	2.45
Gel rubber	Benzene	353.5	177.4	2.91
Sol rubber	Ether	197.8	186.8	0.72
Sol rubber	Benzene	337.8	175.7	2.79

3. Discussion

Ostwald reported that the dipole moment of masticated pale crepe is 14.47 to 45.74×10^{-18} within a range of molecular weights of rubber assumed to be 20,000 to 200,000. (*Kolloid-Z. loc. cit.*) By extrapolation of these values to the case in which the molecular weight is 544.5 as used in this paper, the dipole moment becomes 2.45. Other data of Ostwald are of the same order. Whether or not these coincidences are accidental, it is probable that the impurities of rubber are interlocked mechanically by the rubber molecules and are not combined chemically with the latter, though they are very difficult to remove.

The dipole moment of sol rubber in ether solution is far lower than the others. This does not depend on the kind of solvent. Müller has reported the relation between the dielectric constant of solvent used in measuring polarization and the dipole moment obtained (*Phys. Z.*, **34**, 705 (1933)). From his work, the following formula can be derived.

$$\mu_B = \mu_E [1 - 0.038(\epsilon_B - 1)^2] / [1 - 0.038(\epsilon_E - 1)^2]$$

where μ_B is a dipole moment which should be obtained in benzene solution, μ_E the moment obtained in ether solution, ϵ_B the dielectric constant of benzene and ϵ_E that of ether. By substituting 0.72×10^{-18} for μ_E , 2.288 for ϵ_B , 4.368 for ϵ_E , μ_B becomes 1.19×10^{-18} . This value is still lower than the others. This may be because the sol rubber in ether solution contains chiefly rubber hydrocarbon itself, and the rubber in other solutions is oxidized considerably. Oxygen combined in the long molecule serves to enlarge the dipole moment of rubber. Sol rubber in ether solution is an extract from total rubber, and it has little opportunity to be oxidized, while in other cases, the purified rubber is dried *in vacuo*, weighed in air, and dissolved; this weighing is necessary to ascertain the completeness of drying. The dipole moment obtained by Ostwald and the author seems to be larger than the true value of natural rubber, which should be smaller than the value obtained in sol rubber ether solution in this experiment. Measurements of rubber hydrocarbon which was purified, dissolved, and measured in a completely oxygen-free apparatus will shortly be reported in another paper.

4. Summary

Natural rubber was purified by Pummerer's method and was dissolved in benzene and ether. The dielectric constant, refractive index, density, and concentration of the solutions were determined. From these data, the molecular polarization and dipole moment were calculated on the assumption that the rubber was dissolved in a molecular state of $(C_6H_8)_n$. The dipole moments of total and gel rubber were found to be 2.45 and 2.91×10^{-18} , respectively. These values are of the same

order of magnitude as those of masticated crude rubbers obtained by Ostwald. It may be said that the impurities of rubber are interlocked mechanically on the rubber molecule and are not combined chemically. Sol rubber in ether solution shows a far lower value than the values of total and gel rubber. These latter values may be influenced by autooxidation, and the true value of the rubber hydrocarbon may be far smaller than the result described in this paper.

In conclusion, the author wishes to express his thanks to Professor Yoshio Tanaka for valuable suggestions and criticisms.

Reinforcement and Stearic Acid

Harry Barron

Introduction

In most mixings employed in rubber technology, stearic acid is employed either in virtue of its powers as a softening agent or owing to its being a long chain fatty acid, which removes basic substances, with the formation of soaps.

Claims have been made, however, that it enhances the reinforcing properties of carbon black, and theories have been advanced to account for this. Blake (*Ind. Eng. Chem.*, 20, 1084 (1929)), claimed that it possessed the property of assisting dispersion. He assumed that it was the stearic acid naturally present which ordinarily caused dispersion of carbon black, and not the rubber itself. Applying to this system Langmuir's theory of monomolecular films of fatty acids on water, he showed that the stearic acid naturally occurring in rubber was just sufficient to form a monomolecular layer around the particles contained in a 30-volume loaded mixing, assuming the high value of 0.2μ for the diameter of the carbon black particle. Parkinson (*Trans. Inst. Rubber Ind.*, 5, 279 (1929)) showed this to be untenable, since rubber from which all fatty acids had been removed still dispersed carbon black, which proved that stearic acid had little effect on the dispersion of carbon black in rubber. Depew (*Rubber Age* (N. Y.) 24, 378 (1929)) showed that the dispersion of carbon black in kerosene was unaffected by stearic acid, while Goodwin and Park (*Ind. Eng. Chem.*, 20, 621 (1928)) reported that neither stearic acid nor zinc stearate improved the dispersion of carbon black in rubber or petrol.

The presence of stearic acid in raw rubber was established by Whitby (*India-Rubber Journal*, 68, 617 (1924)), who subsequently studied the effects of removal and addition in relation to the effect of accelerators in different mixings (*J. Soc. Chem. Ind.*, 47, 122 (1928)). Fuller (*Ind. Eng. Chem.*, 21, 723 (1929)) showed that the addition of 1% stearic acid improved the tensile strength and moduli of base mixes containing low grade rubbers. But when added to rubbers containing large amounts of natural acid, there was considerable reduction of these properties. He found that best values were obtained when 1.4% stearic acid was present in the rubber. Dinsmore (*Ind. Eng. Chem.*, 21, 772 (1928)) found that stearic acid added to a base mix caused marked decreases in both the chemical and physical properties. In a stock containing carbon black, the cure was unaltered, but the tensile strength was decreased, while addition of zinc oxide caused acceleration of the cure and increased the tensile properties. He considered that stearic acid decreased the tensile strength and retarded curing, and that zinc stearate played a great part in the stimulation of accelerators, such as mercaptobenzothiazole. Excess of stearic acid retarded the action of diphenylguanidine. North (*Ind. Eng. Chem.*, 31, 725 (1929)) considered that stearic acid aided the dispersion of carbon black.

Experimental

In view of the importance attached to the part played by stearic acid in the functioning of tires, it was considered that light might be thrown on the subject by an investigation into the effect of stearic acid upon the quantities of energy involved in cycles of extension and retraction. The importance attached to the value of the

work of retraction has been stressed by Barron and Cotton (*Trans. Inst. Rubber Ind.*, 7, 209 (1931)).

Mixes containing varying proportions of stearic acid were made up. The base mix employed was:

Rubber	100
Zinc	5
Diphenylguanidine	1.5
Sulfur	3
Carbon black	35

To which were added 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, and 5 parts of stearic acid. An additional mix, the rubber in which had been extracted with acetone for 100 hours in the continuous apparatus described by Marshall (*Chem. News*, 143, 239 (1931))

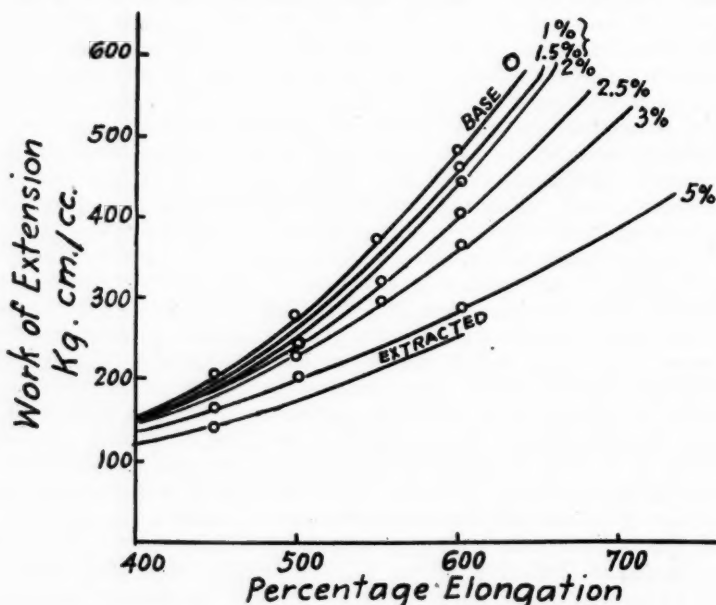


Figure 1—Effect of Stearic Acid on Work of Extension

was also made up. The acetone extract showed that there 1.5% stearic acid was present.

After standing for 48 hours, portions of each mix were vulcanized at 141° C. for different times. Schopper rings were cut from these, and tested for tensile properties. From the values thus obtained, the times of vulcanization corresponding to the maximum tensile properties for each mix were ascertained.

Ten discs of each mix were now cured to the optimum tensile properties. Rings were cut from these, and cycles of extension and retraction carried out as previously described (*loc. cit.*). Stress-elongation diagrams were drawn, and the work of extension, work of retraction, and hysteresis loss were determined planimetrically as described (*loc. cit.*).

From the values obtained, curves were drawn which showed the relationship

between elongation and work of extension, work of retraction, and hysteresis loss, respectively (see Figs. 1, 2, and 3). The values for the work of retraction corresponding to break were obtained by extrapolation of the work of retraction—elongation curves. In this way the hysteresis losses and works of retraction from the breaking point of each mix were obtained, and plotted against the stearic acid present (see Fig. 6).

Results

The results, shown diagrammatically in Fig. 6, indicate that the addition of stearic acid to a carbon black mixing does not appreciably influence the work of extension. That is to say, the reinforcement is unchanged, except that where a certain amount of stearic acid is present the value begins to decrease. However,

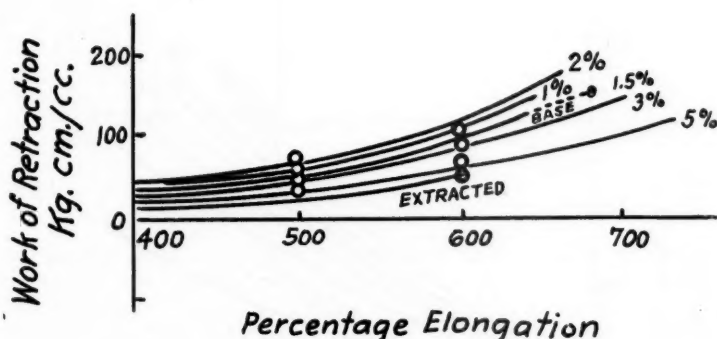


Figure 2—Effect of Stearic Acid on Work of Retraction

stearic acid appears to play a considerable part in the distribution of the work obtained on retraction, and the energy lost as hysteresis. With addition of stearic acid there is a constant decrease in hysteresis loss, while the value of the work of retraction is augmented.

The effect of complete removal of stearic acid is a very large decrease in the reinforcement, despite the fact that the dispersion of carbon black seems unaffected.

EFFECT OF STEARIC ACID IN TENSILE PROPERTIES OF A MIX CONTAINING 20 VOLUMES OF CARBON BLACK

Percentage of Stearic Acid Added	TB Kg. per Sq. Cm.	Percentage Elongation at Break	Work of Extension Kg. Cm./Cc.	Hysteresis Loss Kg. Cm./Cc.	Work of Retraction Kg. Cm./Cc.	Time of Cure Min. at 141 C.
Acetone extracted	154	600	253	202	51	42
0.0	270	640	570	445	123	34
0.5	270	645	570	436	134	34
1.5	275	650	580	425	155	33
2.0	285	660	580	415	165	32
2.5	265	680	545	395	150	32
3.0	255	700	525	385	140	31
5.0	200	730	420	310	110	30
Base mix	180	770	336	256	80	25

Discussion of Results

The effect of adding stearic acid to carbon black mixings is interesting in the light of the theory of reinforcement formulated in a previous paper (*loc. cit.*). There it was suggested in agreement with Hock (*Z. Electrochem. Angew. Phys. Chem.*, 34, 662 (1928)) that reinforcement was composed of two factors, one due to internal friction, and the other due to interfacial tension between rubber and filler. The latter factor was regarded as true reinforcement, and it was considered that the work of retraction is a measure of this true reinforcement. Consequently, it appears that while stearic acid has a small effect upon the total reinforcement, it has a considerable effect upon the reinforcement due to internal friction, this being greatly reduced, while the work of retraction, *i. e.*, the true reinforcement, is increased. Figure 6 indicates the extent to which this occurs.

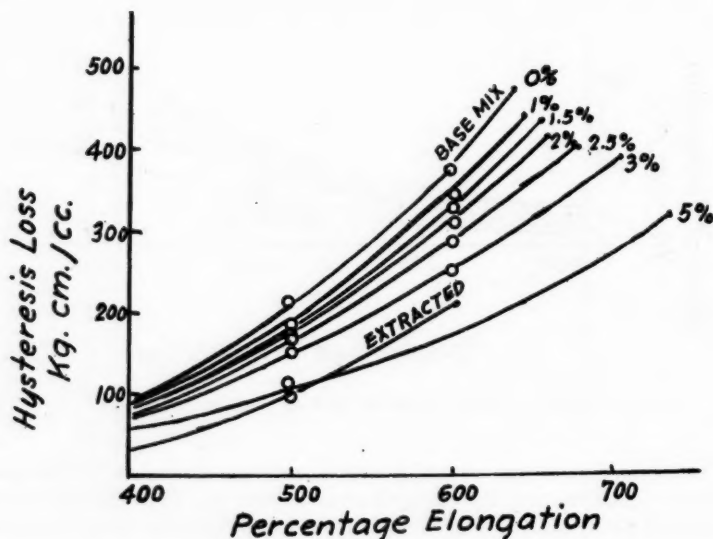


Figure 3—Effect of Stearic Acid on Hysteresis Loss

It appears very likely that stearic acid plays a two-fold part in a rubber mixing. As a softener, it possesses lubricant properties, which cause less friction between different portions of the rubber, and reduce the amount of work which is dissipated in overcoming this internal friction.

The mechanism of the other action is more difficult to explain. However, another well-known property of stearic acid in a rubber mix may assist in the explanation. Stearic acid blooms to the surface of vulcanized rubber on standing in a similar manner to sulfur. It is also soluble in rubber. According to the Gibb's adsorption theory, if a substance dissolves in a medium so as to reduce the interfacial tension of the medium, then there will be a concentration of the dissolved substance at that interface. It seems that such an action may occur in rubber after vulcanization. There will be innumerable interfaces in a rubber mixing, since all filler particles when incorporated into a mix carry a layer of air with them, which is removed by the rubber only if it completely wets the filler surface. Carbon black is

certainly not completely wetted by rubber, that is to say, portions of the particle surface will have thin films of air. Consequently, there must be visualized two types of rubber filler interface, that is to say, a true rubber-filler interface and a

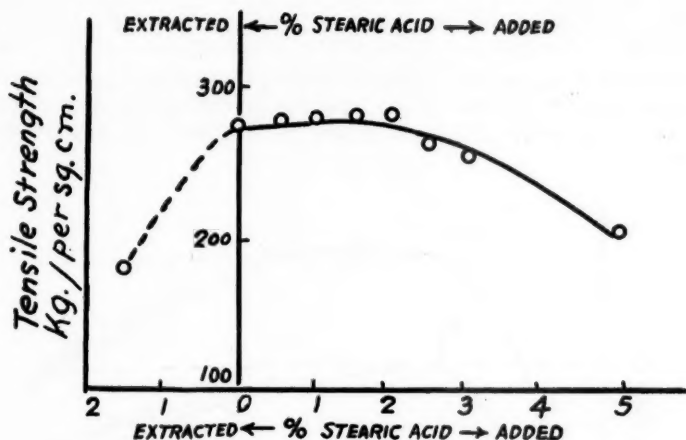


Figure 4—Effect of Stearic Acid on Tensile Strength

rubber-air-filler interface. There is some confirmation of this by Grengquist (*Ind. Eng. Chem.*, 21, 667 (1929)), who found that frozen stretched rubber containing carbon black displayed vacuoles, showing that parts of the filler surface were quite free. Just in the same way that stearic acid blooms to the external surface, so it will

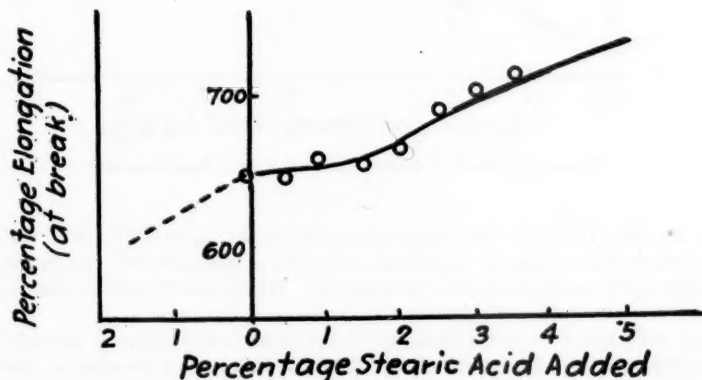


Figure 5—Effect of Stearic Acid on Elongation

bloom to the many internal interfaces. It is a fact that this occurs in sponge rubber. Stearic acid in decreasing the interfacial tension of rubber will cause more efficient wetting by reducing the angle of contact between filler and rubber, in which case the extent of the air films will decrease to a definite limit (since the stearic acid has a limited solubility in rubber). In this way the extent of rubber-filler interface will

increase with addition of stearic acid. That stearic acid does play a considerable part in the reinforcing properties of carbon black is shown by the elimination of reinforcement when acetone extracted rubber, i. e., where all natural stearic acid has been removed, is employed.

It is to be emphasized that this interpretation of the behavior of stearic acid considers it as affecting only the rubber side of the interface by reducing the interfacial tension.

The addition of stearic acid to the mix slightly hastens the time of cure. This is regarded as evidence in favor of the foregoing hypothesis, because retardation of vulcanization by carbon black, according to Wiegand and Snyder (*Ind. Eng.*

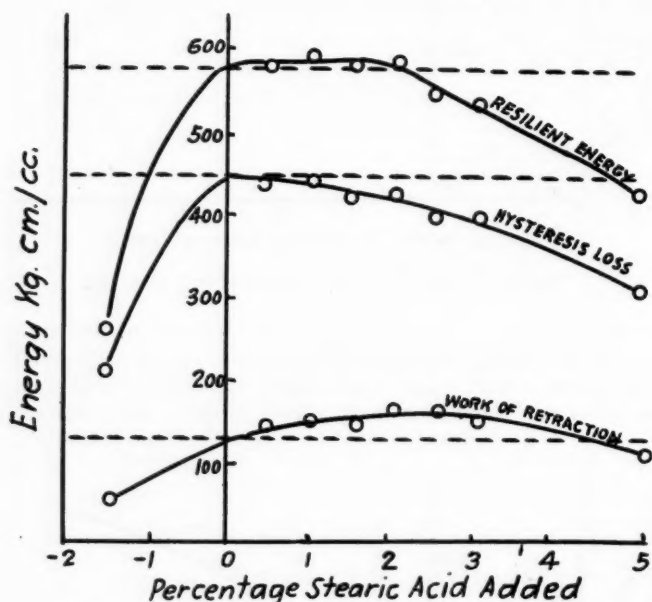


Figure 6—Effect of Stearic Acid on Energy Relationships

Chem., 23, 646 (1931)), is due to adsorption of diphenylguanidine from the rubber. If the interfacial tension is decreased, adsorption is decreased, and consequently more diphenylguanidine remains to function. Where stearic acid is absent, there is considerable retardation of the cure.

When vulcanized rubber containing stearic acid is cut, there is always "blooming" at the new surfaces on standing. This behavior tends to confirm the theory. The considerable time that elapses before it occurs is accounted for by the enormous viscosity of the medium.

Summary of Results and Conclusions

(1) Addition of stearic acid does not increase reinforcement of carbon black mixes to an appreciable extent; however, the work of retraction is considerably augmented, and the hysteresis loss is reduced.

(2) The action is two-fold; free stearic acid lubricates, thereby reducing internal friction, while dissolved stearic acid reduces interfacial tension, thereby increasing wetting or true reinforcement.

(3) Addition of more than 2 per cent of stearic acid lowers reinforcement, since the lubrication effect decreases that portion of reinforcement due to internal friction.

(4) "Blooming" of stearic acid occurs because it decreases surface tension of rubber, and consequently concentrates in the surface.

(5) Removal of stearic acid causes complete disappearance of reinforcement, as measured by work of extension to rupture.

Studies on the Acetone Extraction of Raw Rubber

VII. The Time of Acetone Extraction of Raw Rubber and the Saponification Value of the Acetone Extract and Residue

Hidemaro Endô

LABORATORY OF THE DUNLOP (FAR EAST) COMPANY, KOBE, JAPAN

In this paper the relations between the time of acetone extraction and the saponification value of the acetone extract and of the acetone-extracted residue were studied.

(a) The relations between the time of extraction and the saponification value of the acetone extract in non-continuous extraction.

The procedure was similar to that given in (a) of the experiments in paper (III).

TABLE I

Time of Extraction (Hours)	Sample (G.)	Acetone Extract (G.)	Acetone Extract (%)	0.1 N HCl (Cc.)	Saponification Value (A)	Saponification Value (R)
1	1.5208	0.0488	3.21	1.4	160.6	5.15
2	1.6016	0.0508	3.17	1.6	176.4	5.61
3	1.6100	0.0556	3.45	1.5	151.1	5.22
4	1.5000	0.0510	3.40	1.5	164.7	5.60
5	1.6308	0.0588	3.61	1.6	152.4	5.50
6	1.8970	0.0656	3.46	1.8	153.7	5.47
7	1.8520	0.0640	3.46	1.65	144.2	4.98
8	1.7657	0.0606	3.43	1.55	143.2	4.92
10	1.9032	0.0710	3.73	1.7	134.0	5.00
12	1.9378	0.0666	3.44	1.55	130.2	4.48
14	1.7064	0.0622	3.64	1.45	131.0	4.77
16	1.6364	0.0584	3.57	1.4	134.3	4.79
18	1.4970	0.0576	3.85	1.4	161.1	5.24
20	1.6896	0.0651	3.86	1.55	133.5	5.15
22	1.7084	0.0726	4.25	1.95	150.4	5.40
24	1.7850	0.0764	4.30	2.0	146.6	8.22

(b) The relation between the time of extraction and the saponification value of the acetone-extracted residue in non-continuous extraction.

The acetone-extracted residue from the sample in experiment (a) was dried for 1 hour in a vacuum desiccator, and the saponification value determined.

(c) The relation between the time of extraction and the saponification value of the acetone extract in continuous extraction.

The results for extraction periods up to 8 hours were given in (a), and those for longer than 8 hours are as follows:

(d) The relation between the time of extraction and the saponification value of the acetone-extracted residue in continuous extraction.

The results for extraction periods longer than 8 hours are shown on page 329.

TABLE II

Time of Extraction (Hours)	Sample (G.)	Acetone Extract (G.)	Acetone Extracted Residue (G.)	0.1 N HCl (Cc.)	Saponification Value of Acetone Extracted Residue	Saponification Value (R)
1	1.5208	0.0488	1.4720	0.15	0.57	0.55
2	1.6016	0.0508	1.5508	0.15	0.54	0.54
3	1.6100	0.0556	1.5544	0.15	0.54	0.52
4	1.5000	0.0510	1.4490	0.15	0.58	0.56
5	1.6308	0.0588	1.5720	0.25	0.89	0.86
6	1.8970	0.0656	1.8314	0.25	0.77	0.74
7	1.8520	0.0640	1.7880	0.25	0.78	0.76
8	1.7657	0.0606	1.7051	0.3	0.99	0.95
10	1.9032	0.0710	1.8322	0.1	0.31	0.30
12	1.9378	0.0666	1.8712	0.1	0.30	0.29
14	1.7064	0.0622	1.6442	0.05	0.17	0.16
16	1.6364	0.0584	1.5780	0.05	0.18	0.17
18	1.4970	0.0576	1.4394	0.1	0.39	0.37
20	1.6896	0.0651	1.6245	0.05	0.17	0.17
22	1.7084	0.0726	1.6358	0.15	0.51	0.49
24	1.7850	0.0764	1.7086	0.15	0.49	0.47

TABLE III

Time of Extraction (Hours)	Sample (G.)	Acetone Extract (G.)	Acetone Extract (G.)	0.1 N HCl (Cc.)	Saponification Value (A)	Saponification Value (R)
10	1.8126	0.0670	3.69	1.65	137.9	5.08
12	1.6820	0.0620	3.68	1.5	135.5	4.99
14	1.5692	0.0566	3.61	1.35	133.6	4.82
16	1.8606	0.0670	3.61	1.6	133.7	4.82
18	1.4350	0.0612	4.26	1.45	134.6	5.66
20	1.8000	0.0616	3.42	1.6	145.5	4.98
22	1.6300	0.0550	3.38	1.55	157.8	5.33
24	1.6630	0.0631	3.79	1.7	150.9	5.72

TABLE IV

Time of Extraction (Hours)	Sample (G.)	Acetone Extract (G.)	Acetone Extracted Residue (G.)	0.1 N HCl (Cc.)	Saponification Value of Acetone Extracted Residue	Saponification Value (R)
10	1.8126	0.0670	1.7456	0.3	0.96	0.93
12	1.6820	0.0620	1.6200	0.25	0.86	0.83
14	1.5692	0.0566	1.5126	0.2	0.74	0.71
16	1.8601	0.0670	1.7936	0.1	0.31	0.30
18	1.4350	0.0612	1.3738	0.2	0.81	0.78
20	1.8000	0.0616	1.7384	0.25	0.81	0.78
22	1.6300	0.0550	1.5950	0.25	0.89	0.86
24	1.6630	0.0631	1.5990	0.25	0.88	0.84

TABLE V

Time of extraction (hours)	1	2	3	4	5	6
Saponification value (A)	160.6	176.4	151.1	164.7	152.4	153.7
Acid value (A)	106.7	105.9	103.5	103.7	100.0	102.7
Ester value (A)	53.9	70.5	47.6	61.0	52.4	51.0
Time of extraction (hours)	7	8	10	12	14	
Saponification value (A)	144.2	143.2	134.0	130.2	131.0	
Acid value (A)	102.8	93.3	92.2	88.1	90.7	
Ester value (A)	41.4	49.9	41.8	42.1	40.3	
Time of extraction (hours)	16	18	20	22	24	
Saponification value (A)	134.3	161.1	133.5	150.4	146.6	
Acid value (A)	97.5	94.8	94.9	94.9	95.6	
Ester value (A)	36.8	66.3	38.6	55.5	51.0	

(e) The relation between time of extraction and ester value.

The relation between the time of acetone extraction and the ester value of the acetone extract was studied, non-continuous extraction being selected for this purpose. The ester value (A) is calculated from saponification value and acid value.

Summary of Results

During acetone extraction of pale crepe, the free acids and saponifiable matter were extracted almost completely in 1 or 2 hours. The saponification value (A) had a tendency to decrease rapidly and to reach a minimum after 12 hours (in non-continuous extraction) or after 16 hours (in continuous extraction). The cause of the decrease of the saponification value (A) from the commencement of extraction up to the time mentioned is thought to be due to a gradual increase in the amount of extracted non-acidic compounds and unsaponifiable matter with increasing time of extraction, and to the neutralization of acids by other compounds, as by esterification. After reaching the minimum point, the saponification value (A) had a tendency to increase gradually. This increase is thought to be due to (1) a gradual increase of ester extracted, (2) the formation of acids by oxidation, and (3) the formation of free acids by decompositions of esters, though the last factor does not increase materially the saponification value. The change of saponification value of the acetone extract with increasing time of extraction is not due to any change in the type of compounds gradually extracted, but to a change in the acetone extract in the acetone solution during extraction.

This is in agreement with the acid value. It was observed in a previous paper (III) that almost all of the free acids contained in pale crepe were extracted by acetone in 1 hour. But by extraction for 1 or 2 hours, a small portion of the saponifiable matter still remain unextracted. This remaining part could not be extracted even by prolonged extraction. It is believed, therefore, that the free fatty acids are dissolved in the saponifiable matter, and that the latter are dissolved in the rubber hydrocarbon. As the acetone extract is very labile, so far as the change of acetone extract is concerned, the acetone extract, whether it be dried or left in solution, should not be stored for too long a time. The results obtained by such long extraction by acetone as multiples of ten hours, as used by Whitby and Winn (*J. Soc. Chem. Ind.*, 41, 336T (1923)), are thought to be quite unreliable.

Studies on Chlorinated Rubber

Tatsumi Yamamoto

INDUSTRIAL RESEARCH LABORATORY, MINISTRY OF COMMERCE AND AGRICULTURE, OSAKA, JAPAN

Experiments on the Chlorination of Rubber

As pale crepe, which was used as the raw material, was hard to dissolve in solvent and had a high viscosity, it was first milled for 20 minutes at 80° C. Fifty grams were then dissolved to make a 5 per cent solution in benzene or carbon tetrachloride and placed in 2-liter flasks with 4-hole stoppers. Dry chlorine gas, which was first passed through concentrated sulfuric acid, was passed into the flask at the rate of 200 cc. per second; the outlet tube was connected to a condenser which separated the hydrogen chloride evolved and left the chlorine unchanged; the outlet of the condenser was connected to gas-washing bottles containing aqueous alkali. Thermometers were inserted in the other holes of the stoppers, and the flasks were heated on water baths if necessary.

The temperature increased at first, but diminished as the reaction became slower; the color of the solutions changed from dark brown to light yellow, and the evolution of hydrogen chloride was also evident by fumes in the escaping gases.

After passing the chlorine gas for the required time, air was passed into the flask in order to remove most of the dissolved chlorine and hydrogen chloride in the rubber solution. The solvent was then removed by distilling *in vacuo*. The light yellow reaction product was dissolved in benzene and precipitated by adding ethyl alcohol, was filtered, washed with alkali, and then with water.

The combined chlorine in the samples thus prepared was determined by analysis as silver chloride; the viscosities of samples were determined by an Ostwald viscometer at 30° C. with 5 cc. of solution made by dissolving 0.5 gram in 10 cc. of toluene. The viscosity of distilled water in the same apparatus was 5 seconds. The results are given in Table I.

TABLE I

Sample No.	Solvent	Temperature (° C.)	Time (Hours)	Combined Chlorine (Percentage)	Viscosity (Seconds)	Color of Product
1	C ₆ H ₆	70-80	5	65.6	33	White
2	CCl ₄	22-44	5	59.7	19	Light brown
3	CCl ₄	32-42	7	66.2	20	White
4	CCl ₄	22-44	12	65.3	10	White
5	CCl ₄	70-80	1	38.8	..	Red-brown
6	CCl ₄	70-80	2.5	52.7	54	Light yellow
7	CCl ₄	70-80	5	64.7	18	White
8	CCl ₄	70-80	6	64.6	17	White

With benzene, chlorinated benzene was formed at the same time, and it was difficult to remove from the rubber; this tendency was the same when the temperature of the reaction was changed to 18-35° C. Therefore only carbon tetrachloride was used for the remaining experiments.

The experiment described above was on a laboratory scale to study the chemical properties of the products. For manufacture on a plant scale, the rubber should be milled sufficiently to give concentrated solutions with low viscosities, the solvent should be removed by steam distillation, the product ground to a powder,

the last trace of solvent evaporated by heating at 80°, and the product washed with alkali and then with water. Since part of the carbon tetrachloride escapes as a vapor with an excess of chlorine gas, the condenser must be constructed in such a way as to catch it.

The results indicate that the chlorine contents of the products depend on the time of heating. Sample No. 5, containing 38.8 per cent chlorine, was very unstable and on standing turned to dark brown from reddish brown, and it swelled in the solvent but was not soluble. The color was deeper in samples containing less chlorine. When no heat was applied, the chlorine content reached 66.2 per cent in 7 hours; while at 70–80°, it reached 64.7 per cent in 5 hours, and the chlorine content did not increase by increasing the time of treatment. The product of chlorination was close to a mixture of equal parts of $(C_5H_7Cl)_2$ and $(C_5H_6Cl)_2$, which corresponds to the formula $C_{10}H_{12}Cl_7$, with a chlorine content of 64.7 per cent, representing the addition of 3 and 4 atoms, respectively, of chlorine to isoprene. The viscosity dropped with increasing time, but this may have been the result of a disaggregation of the rubber molecules as the time of chlorination increased.

Hydrogen chloride in the gas-washing bottle which had been evolved from Sample 8 was estimated every 2 hours, and at the end of the experiment the hydrogen chloride dissolved in the rubber solution was washed with water; since this washing also dissolved free chlorine, hydrogen chloride was determined by the difference of total and free chlorine.² Of 49.7 grams of hydrogen chloride evolved, 39.6 grams were evolved in the initial period, 3.6 grams in the middle period, and 3.2 grams in the last period, while 3.3 grams were left in the rubber solution. Thus the evolution of hydrogen chloride was chiefly in the early period of reaction.

The chlorinated rubber, $C_{10}H_{12}Cl_7$, containing 64.7 per cent of chlorine should give off 3 mols. of hydrogen chloride from the substitution of 3 atoms of chlorine, i. e., 39.9 grams of hydrogen chloride from 50 grams of rubber; but the yield of hydrogen chloride was lower than the calculated value. This may have been due to impurities in the rubber and partly to formation of hydrogen chloride from the dissolved chlorine.

The results with different raw rubbers and methods of chlorination are shown in Table II. Samples 9, 10, 15, and 20 were heated on a water bath; Samples 11 and 14 were not heated (temperature of bath).

TABLE II

Sample No.	Raw Material	Solvent	Temperature (° C.)	Time (Hours)	Combined Cl (Percentage)	Viscosity (Minutes)
9	Pale crepe	CCl_4	70–80	4	64.3	17
10	Pale crepe sheet	CCl_4	70–80	4	62.3	48
11	Pale crepe sheet	..	50	8	60.7	21
12	Pale crepe sheet	..	50	9	61.7	20
13	Pale crepe	CCl_4	23–30	3	53.3	..
14	Pale crepe	CCl_4	22–35	4	63.4	34
15	Pale crepe	CCl_4	58–61	2	53.6	185
16	Pale crepe	CCl_4	60–65	3	61.5	19
17	Latex	..	80	9	51.2	..
18	Latex	..	80	10	51.6	..
19	F. A. Q.	CCl_4	70–80	6	64.5	15
20	F. A. Q.	CCl_4	70–80	6.5	65.6	12

Samples Nos. 9, 10, 11, 12, 14, and 16 were white and cotton-like; No. 13 light yellow and cotton-like; Nos. 15, 19, and 20 slightly yellow and cotton-like; Nos. 17 and 18 were light yellow powders.

Sample No. 9 contained 5 per cent of silica gel and sample No. 10 contained 5 per cent of acid clay, but neither of these compounds showed any catalytic action in the

chlorination process. Samples No. 11 and 12 were made in thin sheets 0.25 mm. thick, with talc between to prevent their adhering. They were then cut into threads, placed in the chlorinating apparatus without solvent, and chlorinated by passing chlorine gas and carbon tetrachloride vapor. This method enabled the chlorine to combine with the rubber, and the solvent was saved, but the reaction was not uniform and required a relatively long time.

In Samples Nos. 13 and 16, the rubber solutions were chlorinated under five atmospheres' pressure, with agitation. This method shortened the time of reaction, but it would be difficult to apply on a large scale.

Samples Nos. 17 and 18 were made from 100 cc. of 30 per cent commercial latex diluted to 1 liter with water; the ammonia was neutralized with dilute acetic acid, and the product was then chlorinated. A larger part of the rubber was coagulated, and only a small portion of light yellow powder which swelled in the solvent, but was insoluble and contained approximately 52 per cent of chlorine, was obtained.

Samples Nos. 19 and 20 were made from F. A. Q. sheet instead of pale crepe. The color of the product was slightly poorer than Nos. 17 and 18.

The viscosities of these products were not the same even when they contained the same proportion of chlorine; this might have been due to differences in the disaggregation of the molecules under the different conditions of preparation.

The following experiment was carried out with the object of preventing the escape of unreacted chlorine. The apparatus consisted of two flasks having 4-hole stoppers, with agitators; the outlet tube with the condenser of the first flask was connected to the inlet tube of the second flask, and the chlorination carried out in series. The outlet tube from the first flask contained unreacted chlorine and hydrogen chloride (the presence of hydrogen chloride in the rubber solution gives the hydrochloride of rubber, even at low temperature³). Accordingly the chlorination in series was carried on for 6 hours, a part of the contents in the second flask was then removed, and was chlorinated directly for two more hours. The contents of each flask were saponified with alcoholic sodium hydroxide, and the hydrogen chloride evolved from this reaction was determined. The results are shown in Table III.

TABLE III

Apparatus	Time (Hours)	Combined Cl (Percentage)	Viscosity (Seconds)	HCl (Percentage)	Temperature (° C.)
1st reaction flask	6	64.7	15	2.8	70-80
2nd reaction flask	6	61.2	7	7.5	70-80
2nd reaction flask	8	65.0	16	3.2	70-80

The quantities of hydrogen chloride evolved from the first and second reaction flasks were nearly the same. Rubber hydrochloride might have been formed in the second reaction flask, but since this is unstable, it changed to the chloride. It was thus confirmed that chlorination in series gives the same product as that obtained from direct chlorination.

Properties of the Chlorinated Rubbers

Though there are reports in the literature on the properties of chlorinated rubber, the writer made experiments on certain important properties which have not been described.

Resistance to Chemicals

Samples (1 g.) containing different chlorine contents were made in the form of

pills and were treated in commercial concentrated acids and alkalis at room temperature for ten days. The decreases in weight were as follows:

TABLE IV

Chlorine Content (%)	H ₂ SO ₄ (%)	HCl (%)	HNO ₃ (%)	NaOH (Satd. Soln.) (%)
52.7	2.58
59.7	1.29	1.62	0.53	1.19
64.7	..	0.72	1.20	..
66.2	0.33	0.33	1.10	0.63

The color after treatment with sulfuric acid changed to black in the case of the sample containing 52.7 per cent of chlorine, and to gray in the case of those containing 64.7 and 66.2 per cent of chlorine. There were no changes in color by treatment with other acids and alkali. The resistance to acids (except nitric acid) and alkali increased with increase in chlorine content; those containing over 60 per cent of chlorine showed very high resistances.

Resistance to Heat

The appearance of the products containing different proportions of chlorine after heating at various temperatures is indicated in Table V.

TABLE V

Percentage of Chlorine	100° C.	130° C.	150° C.
38.8	Black
52.7	Black
64.7	No change	Light yellow and soft	Black

The sample containing less chlorine was unstable and that containing 64.7 per cent was stable, and turned soft at 130° C. with slow decomposition; at 150° C. it turned black.

Resistance to Moisture

A sample containing 64.7 per cent of chlorine was dissolved in toluene and spread on a gelatin film over a glass plate and dried. This film was separated by soaking in water. The thickness of the film was 0.01 mm. It was attached to the mouth (20 square cm. in area) of a weighing flask containing 10 cc. of distilled water and sealed with paraffin, was then placed in a desiccator containing concentrated sulfuric acid and kept at 30° C. for 1 hour to test for its permeability to water vapor. The same test was made with a benzylcellulose film, which is said to have the least permeability to water vapor.

Chlorinated rubber film 0.007–0.009 g. per 20 sq. cm. per hour
Benzylcellulose film 0.019 g. per 20 sq. cm. per hour

Less water therefore passed through the chlorinated rubber vapor than through the benzylcellulose. Herbert³ reported that the addition of linseed oil to chlorinated rubber makes its films less permeable to gases.

Stability

The sample containing 64.7 per cent of chlorine and four commercial preparations were tested for chlorine ions by the following method. A two-gram sample was heated in an Erlenmeyer flask containing 100 cc. of water and 3 cc. of ethyl alcohol for 3 hours with reflux condenser, filtered and washed with water until the filtrate measured 200 cc. The turbidity developed by the addition of silver nitrate solution was compared with a standard solution containing a known quantity of chlorine ions. The results are shown in Table VI.

TABLE VI

Sample	Percentage Chlorine Ions	
	1st Extn.	2nd Extn.
Prepared	0.06	0.02
Imported A	0.18	0.04
Imported B	0.06	0.02
Domestic C	0.06	0.01
Domestic D	0.35	0.04

TABLE VII

Sample	Time Required to Change Test Paper Blue (Hours)
1. Prepared	10
2. Imported A	120
3. Imported B	5
4. Domestic C	6
5. Domestic D	4

The chlorine ions ranged from 0.06 to 0.35 per cent, and the proportion decreased by repeating the boiling. Ten grams of a 30 per cent chlorinated rubber solution in xylene were placed in a test tube (1.5 cm. diameter) with a cork stopper and a strip of Congo red test paper, and kept at 100° C. until the test paper turned blue from the hydrogen chloride. The results are indicated in Table VII.

The imported sample A showed extreme stability in comparison with the others. Extraction of sample A with alcohol gave 3 per cent of an oily substance soluble in ether, which was distilled off at 150–160°, and had a pungent odor. It was not identified because of the small quantity. After the addition of 3 per cent of this oil extract and the residue of extraction to the prepared sample 130 hours and 24 hours, respectively, were required before the test paper turned blue. It is evident that the imported sample A contained a stabilizer.

The addition of 1.5 to 3.0 per cent of various amines as stabilizers to the chlorinated rubber gave the following results:

TABLE VIII

Time Required to Change Test Paper Blue (Hours)			Time Required to Change Test Paper Blue (Hours)		
Addition	Percentage		Addition	Percentage	
1 Diphenylamine	3	2	6 Urea	1.5	160
Diphenylamine	1.5	2	7 Triethanolamine	3	49
2 Aniline	3	25	8 Amyl alcohol	3	3
3 Dimethylaniline	3	2	9 Allyl alcohol	3	3
4 Acetanilide	3	1	10 Nothing		10
5 <i>m</i> -Phenylenediamine	3	100	11 Imported sample		120

Aniline, *m*-phenylenediamine, urea, and triethanolamine showed a stabilizing action; urea was the best. The others were injurious to the stability. Experiments to test the stability of varnish, with and without urea, in direct sunlight are in progress.

Chlorinated rubber containing 64.7 per cent of chlorine showed a density of 1.5, 0.2 per cent moisture, and 0.2 per cent ash. It was very soluble in benzene and its homologs, and in carbon disulfide, but was insoluble in alcohol and in gasoline, and swelled in acetone and in ether.

Applications of Chlorinated Rubber

In Varnish.—Since chlorinated rubber has a great resistance to chemicals, it can be used in special varnishes. There is already a commercial product known as "Tornesit." However, as films of chlorinated rubber are weak and brittle, they must be compounded with oil, rosin, or other softening agents.

A mixture of chlorinated rubber 20, diethylphthalate 2, artificial resin varnish 6, and toluene 72, was tested for its flexibility and acid resistance. The varnish dried quickly to a transparent, lustrous film. The flexibility was determined by coating the film on tin plate, drying, wrapping on a glass tube (0.125 inch diameter), and ascertaining the tendency of the film to peel off or crack. The acid resistance was

tested by soaking the sample prepared for the flexibility test in sulfuric acid (d. 1.40) at room temperature for 10 days and examining the external appearance. The Japanese and imported samples showed no cracking in the flexibility test and no change in external appearance after acid treatment.

Application as a Plastic.—If chlorinated rubber can be used as a raw material for plastics, there will be a new demand for it. The following experiment was made with the object of studying this problem.

Chlorinated rubber (containing 64.7 per cent chlorine) was powdered and molded by heating in an iron mold. A preliminary experiment by heating at 125° C. under a pressure of 750 lbs. per sq. inch gave a transparent, light yellow, lustrous plastic mass. Subsequent experiments were carried out with a suitable mold, with mechanical and electrical tests. The results are shown in Table IX. The properties of Bakelite⁴ and ebonite⁵ are shown for comparison.

TABLE IX

	Chlorinated Rubber	Bakelite	Ebonite
Tensile strength (kg. per sq. cm.)	300-377	450	770
Bending strength (kg. per sq. cm.)	632-694	799	...
Puncture voltage (volts per mm.)	36500-41500	16450	79600

The tensile strengths of dumb-bell shaped samples (1 mm. thick and 10 mm. wide at the narrow section) were measured on a Shopper apparatus; the resistance to bending was determined with samples 4 mm. thick, 10 mm. wide, and 70 mm. long with a specially constructed Shopper apparatus.¹ The puncture voltage was made on disc samples 1 mm. thick. According to Table IX chlorinated rubber shows poorer tensile strength than Bakelite and ebonite, less bending resistance than Bakelite, less puncture voltage than ebonite, more puncture voltage than Bakelite, but unlike Bakelite it can be made in any desired color.

Conclusions

1. In the chlorination of rubber, the products have different combined chlorine contents which depend on the time of chlorination, but the final chlorination product seems to be $C_{10}H_{13}Cl_7$, i. e., contains 64.7 per cent of chlorine.

The rubber molecules disaggregate with advancing chlorination and the viscosities diminish. Accordingly the viscosity of rubbers containing the same chlorine contents vary with different conditions of preparation.

2. The properties of chlorinated rubbers vary with differences in their combined chlorine content; for a product to be thermostable and have high resistance to chemicals, it must contain over 60 per cent of chlorine.

3. The best method is to dissolve the pale crepe or F. A. Q. sheet in carbon tetrachloride and pass chlorine through the solution continuously while heating at 70-80°, with agitation. The reaction product is then separated from the solvent by distillation until the last trace of the solvent is removed, and is then washed with water free from acid impurities.

4. Chlorinated rubber has a high resistance to acids and alkalies and, above all, the permeability of films to water vapor is less than that of benzylcellulose. Moreover, chlorinated rubber is not explosive, and burns with difficulty.

5. The stability of four commercial products was studied, and an imported sample which had high stability was found to contain a stabilizer. Among various stabilizers tested, urea had the most beneficial effect.

6. As to the value of chlorinated rubber for varnish, there are many reports, and it is still in an experimental stage; but it has many properties which give

the hope that it may be used as a special varnish after further studies by manufacturers and consumers.

7. By molding powdered chlorinated rubber under pressure and heat, a plastic which was easily removed in a short time was made. Its mechanical and electrical properties were tested and it gave attractive products with many pigments. Chlorinated rubber can be used as substitutes for plastics such as Bakelite or ebonite.

References

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- ³ Treadwell, "Analytical Chemistry," 1919 Edition, Vol. II, p. 324, 655.
- ⁴ Herbert, *Farben-Ztg.*, **38**, 481 (1932).
- ⁵ Sugimoto, *Rpts. Osaka Ind. Research Inst.*, **11**, No. 21, pp. 8 and 10.
- ⁶ Geisler, "Künstlicher Kautschuk für Elektrische Isolierzwecke," 1922 Edition, pp. 57 and 63.

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Determination of Free Sulfur by Titration

B. Faïnberg

ANALYTICAL LABORATORY OF RUBBER DIVISION OF THE "B" EXPERIMENTAL PLANT

In a recent article on the "Iodometric Method of Determination of Free Sulfur" by Bolotnikov and Gurova (*J. Rubber Ind. U. S. S. R.*, 10, 61 (1933); *RUBBER CHEM. AND TECHNOLOGY*, 8, 87 (1935)), the authors described a rapid method for determining free sulfur in rubber without a preliminary extraction.

TABLE I

Number of Analysis	Free Sulfur		Old Method
	Iodometric Titration	(Average)	
1	1.19 }	1.15	1.20
	1.10 }		
2	1.41 }	1.46	1.50
	1.51 }		
3	1.33 }	1.33	1.24
	1.33 }		
4	3.31 }	3.31	3.31
	3.31 }		
5	0.66 }	0.69	0.79
	0.72 }		
6	0.72 }	0.77	0.70
	0.85 }		
7	0.40 }	0.40	0.43
	0.40 }		

TABLE II

Number of Analysis	Free Sulfur		Old Method
	Iodometric Titration	(Average)	
1	0.53 }	0.54	0.73
	0.54 }		
2	0.46 }	0.48	0.64
	0.48 }		
	0.48 }		
3	0.29 }	0.28	0.49
	0.27 }		
	0.27 }		
4	0.24 }	0.23	0.44
	0.22 }		
	0.24 }		
5	0.48 }	0.48	0.51
	0.48 }		
6	0.10 }	0.10	0.13
	0.09 }		
7	0.75	..	1.03

This new iodometric method was tested in determinations of free sulfur in vulcanizates made from synthetic rubber.

A series of analyses were made by the iodometric method, and by the older standard method on vulcanizates with synthetic rubber. Mixtures of very simple compositions were first analyzed, *i. e.*, mixtures of rubber and sulfur and rubber, sulfur, and Agerite antioxidant.

Table I shows some of the results.

Table I shows that the iodometric method and old method give concordant results for free sulfur in simple mixtures.

Analyses of free sulfur were then made on mixtures of soft rubber with fillers. Some of the results are given in Table II.

The results with the mixtures containing fillers are different. There are a few concordant results (tests No. 5 and No. 6), but most of the analyses show low results compared with the old method.

Increasing the time of boiling with sodium sulfite did not change the results. Besides, it was observed in several cases, that during the titration with iodine, the end-point was transitory, and the blue coloration disappeared very quickly.

Accordingly the method of back titration was adopted. A certain excess of iodine was added to the solution, the latter was let stand for 1-2 minutes, and the excess iodine was titrated with sodium thiosulfate.

The results are given in Table III.

TABLE III

Number of Analysis	Free Sulfur	
	Iodometric Titration (Average)	Old Method
1	1.01	1.03
2	0.64	0.69
3	0.71	0.67
4	0.74	0.78
5	0.96	0.99
6	0.78	0.80
7	0.60	0.50
	0.69	..

TABLE IV

Number of Analysis	Free Sulfur	
	Iodometric Titration (Average)	Old Method
1	1.05 } 1.00 }	1.02
2	0.73 } 0.63 }	0.70
3	0.41 } 0.42 }	0.42
4	0.30 } 0.29 }	0.30
5	0.41	..
6	0.13 } 0.10 }	0.12
7	1.90 } 1.91 }	1.90
		2.03

The results given in Table III show that back titration is more satisfactory, and the results check well in the majority of cases. The differences in several cases are not higher than the error allowed for parallel determinations of free sulfur. The parallel results by the iodometric method check very well. In further experiments, back titration was employed.

Free sulfur was determined in vulcanizates of mixtures of synthetic and natural rubber, and of natural rubber alone. (See Table IV).

The results of tests Nos. 1-6 were made on the whole series of vulcanizates from one batch.

It is seen from Table IV that the iodometric method gives good results.

Rubber mixtures containing lead oxide gave trouble in the iodometric titration, because of the fact that lead sulfide had been formed during vulcanization, and when the rubber was boiled with sodium sulfite, the solution turned dark as a result of the lead sulfide forming a colloidal solution. This dark color hindered the titration. To coagulate the lead sulfide, acetic acid (1-2 cc. of 80 per cent) was added to the solution after the rubber was boiled for one hour with sodium sulfite, after which the boiling was continued for one hour more. After filtration, the solution was colorless. The results are shown in Table V.

TABLE V

Number of Analysis	Free Sulfur		Old Method
	Iodometric Titration	(Average)	
1	0.17 } 0.13 }	0.15	0.14
2	0.12	..	0.07
3	0.79 } 0.82 }	0.81	0.97
4	0.30 } 0.33 }	0.32	0.30
5	0.60	..	0.51
6	1.14 } 1.17 }	1.16	1.22
7	0.68	..	0.67
8	0.70	..	0.78

The results of the iodometric titration agree with the results by the old method.

Rubber mixtures containing stearic acid and pine tar sometimes produce turbidity in the solution after boiling with sodium sulfite. After the solution cools and stands, flakes may be formed. In such cases the solutions were cooled by means of ice or ice and salt, NaCl and afterwards filtered. The residue was washed with cold water. Stearic acid usually contains impurities, such as unsaturated acids, and these unsaturated acids, on titration with iodine, increase the percentage of free sulfur. By cooling and filtering, stearic acid and its impurities are removed from the solution.

The results of free sulfur determinations in mixtures with stearic acid, using the method of cooling and filtering the stearic acid, are very satisfactory.

Table VI shows the results with preliminary cooling and filtering.

TABLE VI

Number of Analysis	Free Sulfur		Old Method
	Iodometric Titration	(Average)	
1	1.00 } 0.99 }	1.00	1.03
2	0.89 } 0.90 }	0.90	0.92
3	0.68 } 0.71 }	0.70	0.75
4	1.83 } 1.84 }	1.84	1.91
5	1.73 } 1.69 }	1.71	1.76
6	1.38 } 1.38 }	1.38	1.38
7	1.20 } 1.20 }	1.20	1.20

This iodometric method gives excellent results (as shown in the tables) in a very short time and deserves serious consideration.

Based on the foregoing work, the following conclusions may be drawn:

1. The best method is to employ back titration, allowing the solution to stand for 1 or 2 minutes after addition of iodine.
2. Washing of the rubber and filtrate can be done with cold water.
3. In case the rubber mixture contains lead oxide, concentrated acetic acid should be added to coagulate lead sulfide.
4. To determine free sulfur in vulcanizates containing stearic acid and pine tar, it is necessary to cool the mixture, filter, and wash the residue with cold water.

Effect of Oxygen Absorbers in Rubber

A. A. Somerville

R. T. VANDERBILT COMPANY, NEW YORK, N. Y.

THE oxidation of vulcanized rubber and its deterioration as a result of oxidation are old and well-known phenomena, the outward characteristics of which are loss of tensile strength, brittleness, surface cracking under tension, and an increase in the amount of acetone-soluble material. The rubber increases in weight as oxygen is absorbed. In this species of oxidation, or aging, the oxygen is mostly derived from the atmosphere.

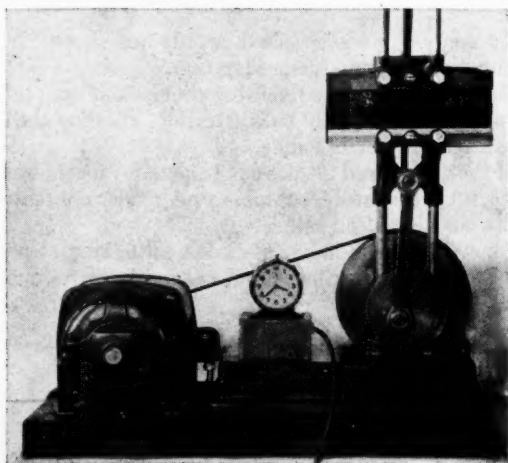


FIGURE 1. DEMATTIA FATIGUE TESTING MACHINE
WITH TEST SPECIMENS

Oxygen Content of Rubber

Much less is known about the oxygen contained in the interior of a piece of vulcanized rubber. That such oxygen exists in rubber goods is generally known. Williams and Neal (6) have determined the amount of oxygen which remains dissolved in pure gum vulcanized rubber under different conditions of temperature and pressure. For example, at 760 mm. and 29° C. (somewhat higher than average room temperature) rubber can hold dissolved 12.5 cc. of oxygen per 100 grams, according to these authors. This is equivalent to about 0.018

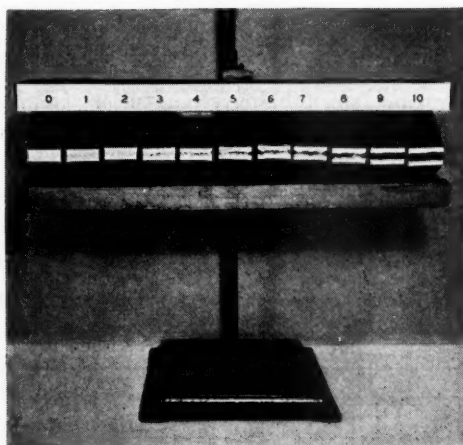


FIGURE 2. SET OF SPECIMENS SHOWING SCALE OF CRACKING

per cent by weight. Besides this, the compounding of rubber with certain pigments and fillers may introduce still greater proportions of oxygen. Carbon black, for instance, is known to contain considerable quantities. The amount of oxygen held by carbon black varies with the source and treatment of

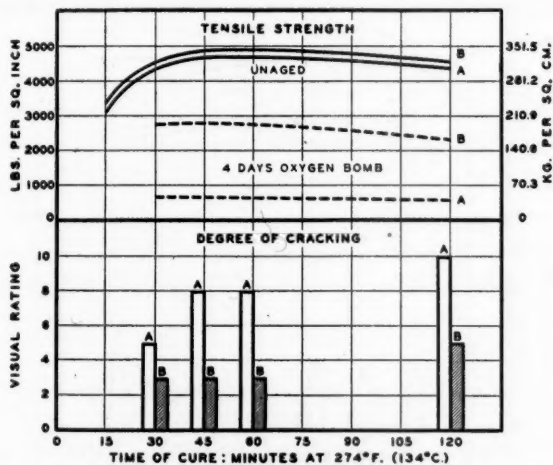


FIGURE 3. EFFECT OF ANTIOXIDANT (AGERITE POWDER) IN A CARBON BLACK STOCK

the material, but Johnson (2) has shown one sample of carbon black to contain 5.76 per cent. The oxygen in carbon black appears to be held in a peculiar state which can be considered neither gaseous adsorption nor chemical combination with the carbon.

It is therefore clear that many rubber compounds made with ordinary compounding ingredients, and particularly with carbon black, may contain appreciable quantities of oxygen. The function and fate of this oxygen in vulcanization and during the subsequent life of the rubber is obscure and speculative

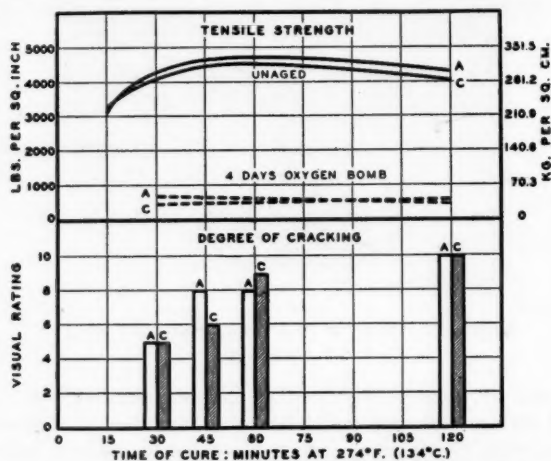


FIGURE 4. EFFECT OF AN OXYGEN ABSORBER (PYROGALLOL-ETHANOLAMINE)

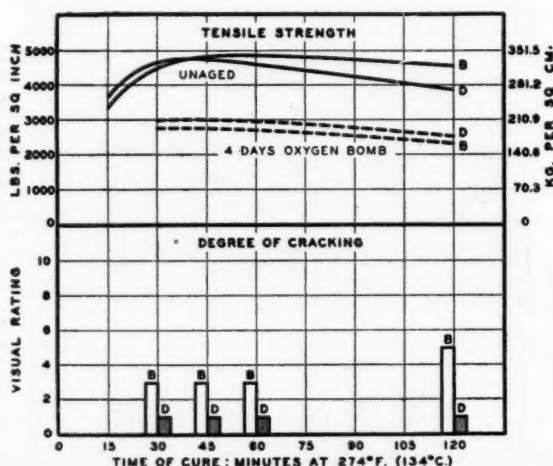


FIGURE 5. EFFECT OF AGErite POWDER PLUS PYROGALLOL-ETHANOLAMINE

but it is not unreasonable to suppose that it must have a bearing on the aging properties and service obtainable from the rubber article. It is well known that carbon black compounds age more rapidly than similar compounds made with other fillers, or with none. It is probable that this poor aging property of carbon black, which offsets to a considerable extent

its other valuable qualities, is related in some way to its appreciable oxygen content.

Besides the usual manifestations of deterioration in rubber goods, such as tensile loss and brittleness, there is another well known in articles subjected in service to often repeated

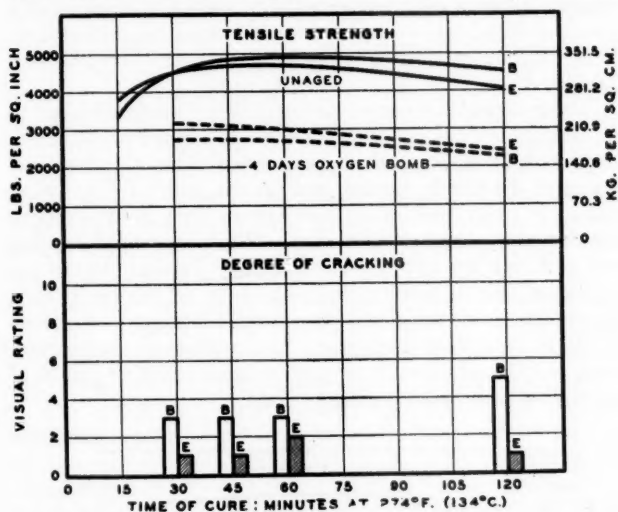


FIGURE 6. EFFECT OF AGERITE POWDER PLUS PYROGALLOL-QUINOL-ETHANOLAMINE

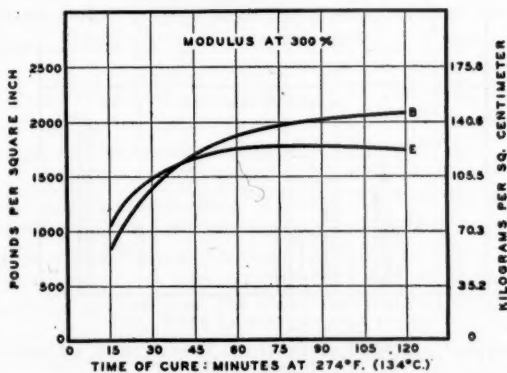


FIGURE 7. EFFECT OF PYROGALLOL-ETHANOLAMINE ON MODULUS

dynamic strain such as bending or stretching, but which does not appear in those that remain at rest. This defect is known as flex-cracking. The rubber surface in the region of the bending or flexure gradually develops small cracks. As flexing continues, these cracks increase in length and depth and in time will traverse the whole thickness of the rubber,

which is not necessarily deteriorated in the ordinary sense of the word. Flex-cracking is a defect found most commonly in tire treads and side walls, conveyor belt covers, footwear uppers, and rubber soling—all articles in which continued flexing forms an important part of the service which they must deliver. From a commercial point of view flex-cracking is a serious defect because, apart from its effect on appearance, it may ruin an article long before its useful span of life has been completed.

Flex-cracking has become a particularly acute problem in the tire industry in the last 5 or 6 years because of (1) structural changes in tires, which have accentuated the degree of flexing of the tire in service, and (2) the gradually increased loading of tread compounds with carbon black in attempts to improve the abrasion resistance. While increased loading with carbon black has largely solved the problem of abrasion resistance, this success has been offset by an increased tendency to flex-crack, which has prevented still larger proportions of carbon black from being used. Larger proportions of carbon black would undoubtedly be used if more effective means of controlling flex-cracking were available.

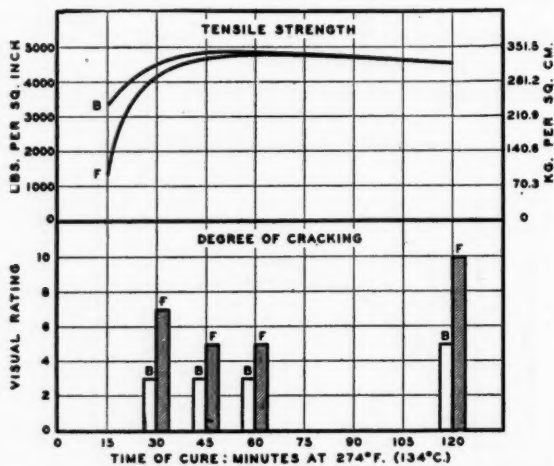


FIGURE 8. EFFECT OF BENZOYL PEROXIDE IN A CARBON BLACK STOCK

Causes of Flex-Cracking

Neal and Northam (4) have studied flexing in nitrogen, oxygen, air, and ozonized air, and have shown that cracking is due to oxidation rather than to mechanical fatigue or to the possible production of minute quantities of ozone by static electric discharges at the points of flexure. Neal and Northam found that the rates of deterioration on flexing in air and in

oxygen were approximately the same; that deterioration in nitrogen was very much slower than in air or oxygen; and that the addition of an antioxidant (phenyl- β -naphthylamine) protected the rubber in air or oxygen but not in nitrogen. These authors concluded that the effectiveness of the antioxidant probably lies in its retarding action on oxidation of the rubber by external oxygen and that no effect could be expected from the antioxidant in an atmosphere of nitrogen. They explain the fact that deterioration (cracking) of the rubber in nitrogen, though much slower than in air or oxygen, did finally set in, by pointing out that the rubber contained some oxygen dissolved¹ and also adsorbed on the pigments.

The amount of oxygen which rubber can hold dissolved under ordinary conditions is very small, but compounding ingredients, especially carbon black, may carry into the rubber much larger amounts. The important point is that these investigations have brought out the significance of oxygen held within the rubber as distinguished from atmospheric oxygen in contact with the rubber surface. The ordinary antioxidant tends to prevent deterioration due to the latter but does not seem to offer much protection against the former.

The use of antioxidants has been to date the principal chemical means of combating flex-cracking. Some of these agents—for example, phenyl- β -naphthylamine—exercise considerable protective action against flex-cracking while others have little or no effect—for example, *sym*-dinaphthyl-*p*-phenylenediamine. The fact that some materials, which have good antioxidant properties, have little effect on flex-cracking proves that flex-cracking and deterioration are separate and distinct problems. The selection and use of age-resisters for various purposes, including resistance to flex-cracking, have been described by Crawford (1). Other factors also have a bearing on the resistance of rubber to flex-cracking. Street (5) has discussed the harmful effect of grit in carbon black. This, however, is a mechanical rather than a chemical effect. It is obvious that, to obtain the best flex-cracking resistance from any given compound, the ingredients should be as free from hard or coarse particles as possible.

Taking these facts into consideration, and particularly that commercial antioxidants act chiefly catalytically (3) to prevent oxidation and do not appreciably absorb oxygen, the author believed that, if means could be found of absorbing or removing the oxygen dissolved or held in the rubber, a greater degree of resistance to flex-cracking than that obtained from an antioxidant alone might possibly be accomplished.

Many preliminary experiments were made. Batches of tread stock were exposed to vacuum treatment, others were

¹ These authors quote Williams and Neal (6) as having shown that at 37° C. the solubility of oxygen in rubber is greater than 1.0 per cent. This is evidently a misquotation because the data in the article of Williams and Neal show the solubility of oxygen in rubber at atmospheric pressure and ordinary temperature to be of the order of 0.018 per cent.

compounded with metallic powders and combinations, such as zinc, iron, and lead powders, and aluminum amalgam. Others again were treated with such oxygen-absorbing materials as yellow phosphorus and benzaldehyde. Many of these tests brought negative results, but a sufficient number of them showed enough improvement over the effect of the antioxidant to warrant the belief that the idea of oxygen absorp-

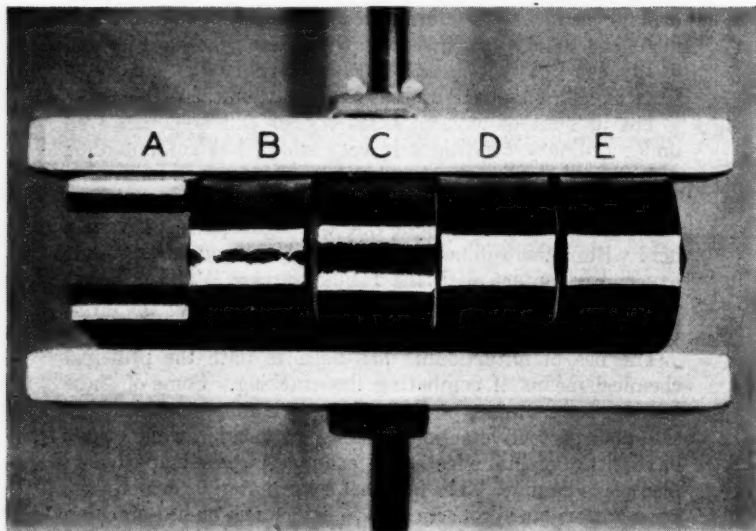


FIGURE 9. SPECIMENS CURED 120 MINUTES AND FLEXED 150,000 CYCLES

- | | |
|----------------------------------|--|
| A. Blank without antioxidant | D. Antioxidant plus pyrogallol-ethanolamine |
| B. With antioxidant alone | E. Antioxidant plus pyrogallol-quinol-ethanolamine |
| C. Pyrogallol-ethanolamine alone | |

tion within the batch would provide a sure means of controlling flex-cracking, if a practical and efficient oxygen-absorbing medium could be found.

Organic Oxygen Absorbers

The development of a practical solution of the problem has been completed within the last year in the use of certain oxygen absorbers or strong reducing agents, among which the substances known as photographic developers are particularly useful. The object of this paper is to describe the application of these materials in rubber compounds and to show their effectiveness in reducing the tendency to flex-crack.

Photographic Developers

Modern photographic developers have different oxygen-absorption rates. It was found that those which in an alkaline solution absorbed oxygen most powerfully also had the greatest effect in retarding flex-cracking. The most efficient

were found to be (1) pyrogallol and (2) quinol (hydroquinone). On the basis of equal weights, pyrogallol absorbs oxygen roughly four times faster than quinol. It has considerably

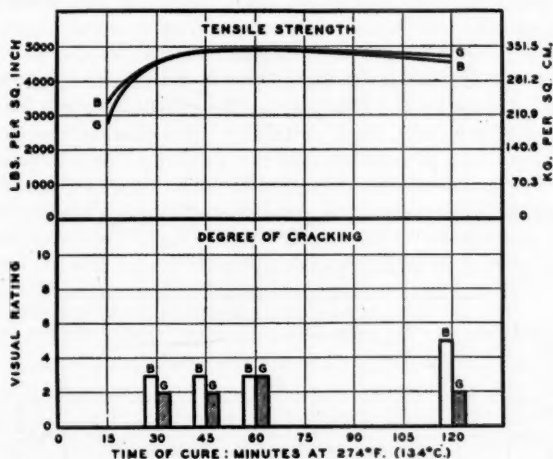


FIGURE 10. EFFECT OF PYROGALLOL-ETHANOLAMINE IN PRESENCE OF BENZOYL PEROXIDE

greater effectiveness in reducing flex-cracking; hence most of the data shown here are those obtained with pyrogallol.

Pyrogallol and Quinol

Both pyrogallol and quinol have been referred to in the

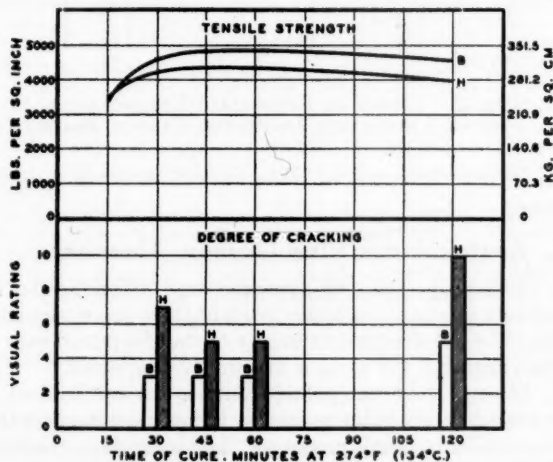


FIGURE 11. EFFECT OF INCREASED CARBON BLACK

literature as antioxidants, and the latter seems to have been used as such to a limited extent. Numerous bomb aging tests made in this laboratory, however, have failed to show that

pyrogallol has any age-resisting properties. This oxygen absorber cannot therefore be regarded as an antioxidant for rubber in the modernly accepted sense of the word. Pyrogallol has practically no oxygen-absorbing capacity except in an alkaline medium; hence, if it is to be used as an absorber of oxygen in rubber, a suitable organic base must also be provided. Numerous bases have been found effective, but the most satisfactory and practical are the ethanolamines. These are nonvolatile and, being extremely water-soluble, they tend to carry traces of moisture into the mix which help to render the pyrogallol-ethanolamine combination oxygen-absorbent. Pyrogallol alone has a strong retarding effect on vulcanization. This retardation is overcome by the base, the proportion of which may be adjusted to compensate for the loss of curing

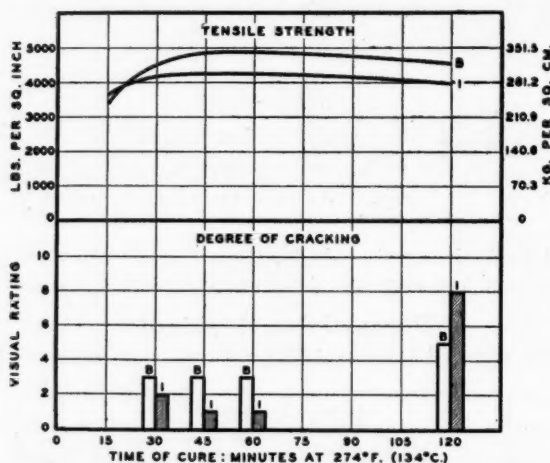


FIGURE 12. EFFECT OF PYROGALLOL-ETHANOLAMINE IN A STOCK CONTAINING INCREASED CARBON BLACK

speed in most compounds. The base thus serves a double purpose.

Antioxidants Plus Oxygen Absorbers

If small proportions of pyrogallol and ethanolamine are added to a mix without an antioxidant, they have very little effect. The flex-cracking tendency of the compound may be reduced slightly; the aging is practically unaffected.

If, however, the compound contains an antioxidant, a very great increase in the resistance to flex-cracking over that due to the antioxidant is produced. This increase in resistance to flex-cracking produced by the pyrogallol-ethanolamine combination has been found with most of the strong commercial antioxidants. In most cases the improvement is far greater than can be produced by largely increasing the dosage of antioxidant. Outstanding results are therefore obtained only

when the following combination of materials is used: a catalytic antioxidant, an oxygen absorber, and an organic base.

If quinol is substituted for pyrogallol, a smaller increase in the resistance to flex-cracking over that obtained by the antioxidant alone is produced. Quinol, however, may be partially substituted for pyrogallol without noticeable diminution of the effect of the latter. Quinol has a slight accelerating effect on the rate of cure, while pyrogallol retards strongly. Partial substitution of the pyrogallol by quinol has therefore some advantage from the point of view of curing rate.

The proportions of oxygen absorber and base required to produce the maximum effect are small and together do not need to exceed the amount of antioxidant used. Thus, with 1 per cent of antioxidant—a commonly used proportion—not over 0.5 to 1 per cent of pyrogallol together with 0.25 to 0.5 per cent of ethanolamine needs to be used.

The data given later show the effect of pyrogallol and a mixture of pyrogallol and quinol in a typical carbon black tread compound. Carbon black compounds are used for flex-cracking tests because most of the rubber goods which are subject to flex-cracking are made from carbon black compounds. Increasing the amount of carbon causes increased tendency to crack, so that it is highly desirable to have a means of minimizing or substantially reducing the cracking tendency.

The tests for flex-cracking tendency were all made on a DeMattia fatigue testing machine (Figure 1):

The test pieces consisted of mold-cured strips, 75 mm. wide, 6 mm. thick, and 150 mm. long, having a half-round groove of 3-mm. radius across the middle of the strip to act as a flexing zone in simulation of the depression in a nonskid tire tread. The test strips were set in the jaws of the machine, twelve at a time, with no initial stretch, and flexed through an angle of 180° at the grooves; these were the outer or stretched surfaces when the strips were bent double.

In the case of tread and other high-grade carbon black stocks the strips were examined after 50,000, 100,000, and 150,000 flexing cycles, and the degree of cracking of each specimen was visually estimated.

In judging the degree of cracking of the flexed specimens, an arbitrary scale of 0 to 10 was used; 0 represented the condition of a fresh or uncracked specimen, and 10 indicated that the specimen was completely cracked through. Figure 2 represents a set of specimens which show the scale of cracking from 0 to 10. The grooves were painted white while the strips were straightened to close the cracks. On bending them back again the cracks appear to good advantage.

Usually four cures from each compound, including a slight undercure and an overcure, were flexed. In Table I the numerical values assigned to the specimens after each examination (flexing period) are given by cures in three columns representing the three flexing periods. The sum total of the four values in any column, therefore, gives in an approximate way the condition of the stock as a whole after the number of

flexures indicated above that column. By studying the sum totals of the columns, an easier comparison of different compounds can be made than by studying the individual values for each cure.

Compound *A* represents a typical carbon black tread stock without an antioxidant. It ages poorly, as shown by the oxygen bomb test, and develops cracks readily when flexed.

B shows the effect of adding an antioxidant (phenyl- β -naphthylamine), a substantial improvement in the resistance of the compound to both aging and flex-cracking results. Figure 3 gives a graphical comparison of *A* and *B*.

C shows the effect of adding the oxygen-absorbing combination, pyrogallol-ethanolamine, without any antioxidant; there is no improvement in aging over the original blank stock, *A*, and the resistance to flex-cracking is only slightly better than that of the blank. The oxygen absorber has therefore no antioxidant power. Figure 4 compares *A* and *C*.

In compound *D* the oxygen-absorbing combination is used together with the antioxidant; here the aging resistance imparted by the antioxidant is unimpaired (if anything, slightly enhanced), and the tendency to flex-cracking is greatly reduced. *B* and *D* are compared in Figure 5.

E is another example of the combined use of antioxidant and oxygen absorber; the latter is a combination of pyrogallol, quinol, and ethanolamine. The mixture of pyrogallol and quinol retards the rate of cure less than does pyrogallol, so that a smaller proportion of ethanolamine is required for adjustment. The effect of the mixture on flex-cracking tendency is practically the same as that of pyrogallol. Figure 6 compares *B* and *E*.

In Figure 7 the modulus curves of *B* and *E* are compared. The oxygen-absorbing combination has the effect of slightly increasing the modulus in the early cures and lowering it in the longer cures, so that the curves cross.

Figure 9 shows photographically the comparative resistance of the five compounds *A*, *B*, *C*, *D*, and *E* to flex-cracking. The specimens were 120-minute cures which had received 150,000 flexings. The effect of the oxygen-absorbing combinations in *D* and *E* is striking; the specimens were painted white before photographing to show the cracks.

Effect of Oxygen Absorber with Added Oxidizing Agent

The flex-cracking tendency of a stock may be purposely increased by the addition of a substance which can liberate oxygen. Benzoyl peroxide is a suitable organic material. It has a slight retarding effect on the rate of cure, but increases the modulus somewhat and the flex-cracking tendency markedly, presumably because of liberation of oxygen within the rubber. Now if a pyrogallol-ethanolamine mixture is added to the stock containing benzoyl peroxide, the effect of the

TABLE I. EFFECT OF ANTIOXIDANT ALONE, OXYGEN ABSORBER ALONE, AND ANTIOXIDANT PLUS OXYGEN ABSORBER

Press cures at 274° F. (134° C.)	M.in.	Tensile Properties ^a before Aging														
		a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
Smoked sheets																
Stearic acid																
Pine tar																
Zinc oxide																
Carbon black																
Sulfur																
Mercaptobenzothiazole (Captax)																
Phenyl-β-naphthylamine (Agerite Powder)																
Pyrogallol																
Quinol																
Ethanolamine																
Total																

Tensile Properties ^a after 4 Days of Aging in Oxygen Bomb [70° C. (158° F.) and 300 Pounds per Square Inch Pressure]														
680	3090	640	820	3320	630	980	3220	580	1095	3620	585	1030	3750	630
1205	4320	610	1395	4320	605	1355	4180	610	1485	4720	595	1495	4510	590
45	1555	580	1715	4850	580	1560	4390	580	1640	4690	575	1685	4630	585
60	1730	580	1835	4860	550	1550	4580	570	1720	4600	530	1780	4740	580
90	1950	505	2010	4750	530	1635	4300	565	1715	4300	530	1730	4360	545
120	2110	440	2030	4570	515	1700	4070	560	1675	3860	520	1760	4120	530

Flex-Crack Rating (Unaged), 50,000, 100,000, and 150,000 Flexures on DeMattia Machine														
570	385	1035	2750	585	470	240	1520	2960	540	1410	3140	545	3140	545
610	680	1300	2760	545	465	210	1560	3030	530	1550	3110	535
45	285	1450	2700	500	455	190	1700	2830	480	1680	2960	480
60	560	1690	2330	500	590	180	1760	2500	430	1735	2360	400
120	..	575	220	1690

Flex-Crack Rating (Unaged), 50,000, 100,000, and 150,000 Flexures on DeMattia Machine														
1	3	5	1	2	3	1	3	5	0	0	1	0	0	1
2	6	8	0	2	3	1	6	6	0	0	1	1	0	1
3	8	8	0	2	3	2	6	9	0	0	1	1	0	1
4	5	8	0	2	3	2	6	10	0	0	1	1	0	1
5	10	10	1	2	5	2	10	30	0	0	1	1	0	1
6	8	10	1	2	5	2	10	30	0	0	1	1	0	1
7	10	10	1	2	5	2	10	30	0	0	1	1	0	1
8	10	10	1	2	5	2	10	30	0	0	1	1	0	1
9	10	10	1	2	5	2	10	30	0	0	1	1	0	1
10	10	10	1	2	5	2	10	30	0	0	1	1	0	1
11	10	10	1	2	5	2	10	30	0	0	1	1	0	1
12	10	10	1	2	5	2	10	30	0	0	1	1	0	1
13	24	31	2	8	14	6	18	30	0	1	4	0	1	3
Total	13	24	31	2	8	14	18	30	0	1	4	0	1	3

^a a = stress at 300 per cent, pounds per square inch; b = tensile strength, pounds per square inch; c = elongation at break, per cent.

latter is almost completely eliminated and the stock shows little more tendency to crack than if benzoyl peroxide had not been added. This artificial production of increased crack-

TABLE II. EFFECT OF BENZOYL PEROXIDE WITH AND WITHOUT OXYGEN ABSORBER

	B	F	G
Smoked sheets	100	100	100
Stearic acid	4	4	4
Pine tar	2	2	2
Zinc oxide	5	5	5
Carbon black	45	45	45
Sulfur	3	3	3
Captax	1	1	1
AgeRite powder	1	1	1
Benzoyl peroxide	..	2	2
Pyrogallol	1
Ethanolamine	0.5
Total	161	163	164.5

Tensile Properties^a

Press cures
at 274° F.
(134° C.)

Min.	a	b	c	a	b	c	a	b	c
15	820	3320	630	320	1305	570	830	2710	560
30	1395	4520	605	1195	4190	635	1530	4530	610
45	1715	4850	580	1655	4640	590	1820	4850	595
60	1835	4960	550	2030	4870	565	2000	4810	570
90	2010	4750	530	2370	4680	500	2170	4870	550
120	2080	4570	515	2700	4570	450	2240	4700	530
Flex-Crack Rating, 50,000, 100,000, and 150,000 Flexures on DeMattia Machine									
30	1	2	3	1	3	7	0	1	2
45	0	2	3	1	3	5	0	0	2
60	0	2	3	1	3	5	0	2	3
120	1	2	5	10	10	10	0	0	2
Total	2	8	14	13	19	27	0	3	9

^a a = stress at 300 per cent, pounds per square inch; b = tensile strength, pounds per square inch; c = elongation at break, per cent.

ing tendency and its correction by the addition of an oxygen-absorber tends to corroborate the theory that dissolved and/or adsorbed oxygen plays an important part in flex-cracking.

The data in Table II show the effect of benzoyl peroxide, with and without an oxygen-absorber. These results are shown graphically in Figures 8 and 10.

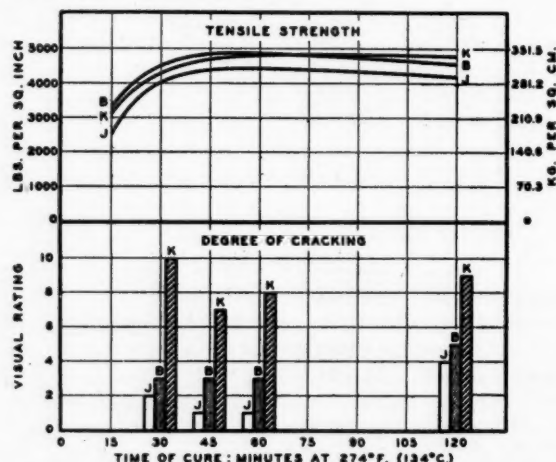


FIGURE 13. EFFECT OF DIFFERENT SULFUR RATIOS

Increased Carbon Black and Flex-Cracking

Carbon black is the only known reënforcing filler which produces high resistance to abrasion. Attempts to increase the carbon black loading beyond the present commercial dosage of 45 to 50 per cent on the rubber have been unsuccessful for

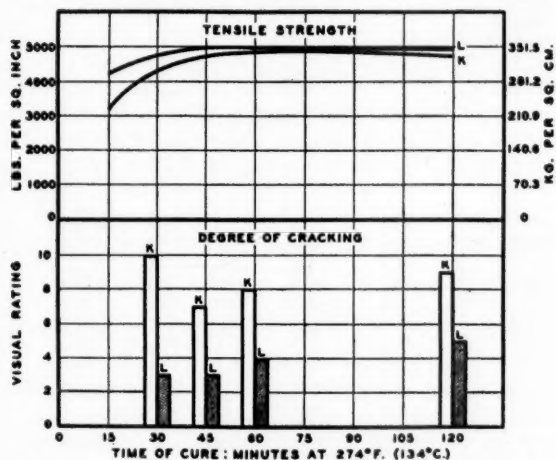


FIGURE 14. EFFECT OF PYROGALLOL-QUINOL-ETHANOLAMINE IN A LOW-SULFUR STOCK

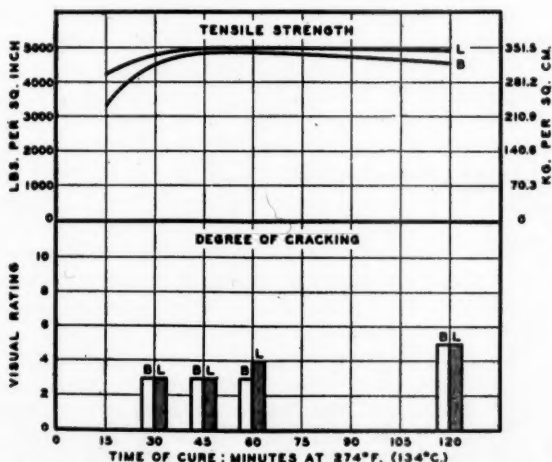


FIGURE 15. COMPARISON OF LOW-SULFUR STOCK CONTAINING OXYGEN ABSORBER WITH NORMAL-SULFUR STOCK WITHOUT OXYGEN ABSORBER

articles such as tire treads, on account of the increased tendency of the compounds to flex-crack in service. The antioxidants in present commercial use, while capable of exerting a considerable reduction in the cracking tendency, are not

TABLE III. EFFECT OF INCREASED CARBON BLACK WITH AND WITHOUT OXYGEN ABSORBER

	B	H	I
Smoked sheets	100	100	100
Stearic acid	4	6	6
Pine tar	2	2	2
Zinc oxide	5	5	5
Sulfur	3	3	3
Captax	1	1	1
Carbon black	45	60	60
AgeRite Powder	1	1	1
Pyrogallol	0.75
Ethanolamine	0.5
Total	161	178	179.25

Tensile Properties^a

Press cures at 274° F. (134° C.)										
Min.		c	a	b	c	a	b			
15	820	3320	630	1175	3520	600	1360	3610	600	
30	1395	4520	605	1885	4200	555	1870	4150	570	
45	1715	4850	580	2380	4250	510	2250	4250	525	
60	1835	4860	550	2570	4250	470	2380	4220	500	
90	2010	4750	530	2950	4110	420	2560	4100	440	
120	2080	4570	515	3130	4000	375	2660	3990	425	
Flex-Crack Rating, 50,000, 100,000, and 150,000 Flexures on DeMattia Machine										
30	1	2	3	2	4	7	0	0	2	
45	0	2	3	1	3	5	0	0	1	
60	0	2	3	1	3	5	0	1	1	
120	1	2	5	10	10	10	0	6	8	
Total	2	8	14	14	20	27	0	7	12	

^a a = stress at 300 per cent, pounds per square inch; b = tensile strength, pounds per square inch; c = elongation at break, per cent.

TABLE IV. EFFECT OF DIFFERENT SULFUR RATIOS
(Low sulfur with and without oxygen absorber)

	J	B	K	L
Smoked sheets	100	100	100	100
Stearic acid	4	4	4	4
Pine tar	2	2	2	2
Zinc oxide	5	5	5	5
Carbon black	45	45	45	45
AgeRite Powder	1	1	1	1
Sulfur	6	3	1.5	1.5
Captax	0.5	1	1	1
Tuads (tetramethylthiuram disulfide)	0.1	0.1
Vandex (selenium)	0.15	0.15
Pyrogallol	0.5
Quinol	0.25
Ethanolamine	0.25
Total	163.5	161	159.75	160.75

Tensile Properties^a

Press cures at 274° F. (134° C.)		Resin Properties										
Min.		a	b	c	a	b	c	a	b	c	a	b
15	545	2510	635	820	3320	630	625	3150	710	1010	4230	670
30	1035	4060	635	1295	4520	605	1100	4310	635	1400	4750	640
45	1415	4420	590	1715	4850	580	1570	4700	595	1670	5000	610
60	1620	4400	575	1835	4860	550	1680	4840	580	1720	4970	585
90	1990	4310	500	2010	4750	530	1890	4850	575	1760	4950	580
120	2070	4210	495	2080	4570	515	1980	4790	535	1795	4920	570
Flex-Crack Rating, 50,000, 100,000, and 150,000 Flexures on DeMattia Machine												
30	0	1	2	1	2	3	2	3	10	1	1	3
45	0	0	1	0	2	3	1	3	7	1	2	3
60	0	0	1	0	2	3	1	3	8	1	2	4
120	0	0	4	1	2	5	1	4	9	1	3	5
Total	0	1	8	2	8	14	5	13	34	4	8	15

^a a = stress at 300 per cent, pounds per square inch; b = tensile strength, pounds per square inch; c = elongation at break, per cent.

strong enough to allow further substantial increases in the carbon black ratio.

If an oxygen absorber such as pyrogallol-ethanolamine is used together with the antioxidant, the tendency to flex-crack is so diminished that substantial carbon black increases may be made without incurring excessive cracking. This fact may be of some importance to the tire industry which is continually seeking greater abrasive resistance in tread compounds. The results given in Table III on compounds *B*, *H*, and *I* show the effect on flex-cracking of 60 parts of carbon black as compared with 45 per 100 parts of rubber and also the effect of adding an oxygen absorber to the 60 per cent black stock. These results are shown graphically in Figures 11 and 12.

Relation of Sulfur Ratio to Flex-Cracking

One of the objections to carbon black compounds of the low-sulfur type has been their increased tendency to flex-crack. This has tended to restrict the application of such compounds to articles which are not severely flexed in service. Investigation has shown that there is a well-marked relationship between the amount of sulfur used for vulcanization and the tendency to crack. For a given compound the flex-cracking tendency varies inversely with the amount of sulfur used; that is, the higher the sulfur ratio (within reasonable limits) the less pronounced is the cracking.

Substantial increases in the sulfur ratio of a tread compound would therefore markedly reduce the cracking, but this is not a practical procedure because the tendencies to deterioration and sulfur bloom both increase when the sulfur ratio is raised. The addition of higher proportions of antioxidant does not usually bring the cracking tendency of a low-sulfur stock down to the same level as that of a normal-sulfur compound. This, however, can be accomplished by the use of an oxygen absorber with the antioxidant.

Compounds *J*, *B*, *K*, and *L* (Table IV) show the effect of high and low sulfur, as compared with normal sulfur, on flex-cracking, and also the effect of an oxygen absorber in the low-sulfur compound. The low-sulfur compound containing antioxidant plus oxygen absorber has practically the same flex-crack rating as the normal sulfur compound containing antioxidant but no oxygen absorber. These results are shown graphically in Figures 13, 14, and 15.

Conclusions

In this discussion of flex-cracking, its causes, and a means of controlling it, the theory that oxidation of the rubber is the main factor involved has been used as a foundation. No attempt has been made to prove chemically that oxidation of the rubber actually takes place. This would be difficult,

since flex-cracked rubber does not necessarily show the ordinary signs of deterioration, but the work of Neal and Northam (4) has indicated that oxygen plays a part.

The facts that oxygen absorbers definitely retard flex-cracking and also that the more strongly they are able to absorb oxygen, the greater is their retarding effect, would be difficult to explain on any other basis. The mechanism of the reaction, however, is obscure and is further complicated by the fact that the oxygen absorbers develop their full effect only in the presence of a catalytic antioxidant. As a working hypothesis it may be assumed that the oxygen absorber removes dissolved or absorbed oxygen within the rubber before and during vulcanization, while the antioxidant protects the rubber surface against atmospheric oxygen during service. It is realized that this hypothesis does not explain every fact connected with the use of oxygen absorbers to complete satisfaction and will doubtless be subject to change or modification as practical experience with these agents accumulates. In the meantime it is believed that a practical commercial means of greatly retarding the flex-cracking tendency of rubber goods has been developed.

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Hydrazines as Rubber Softeners

I. Williams and C. C. Smith

E. I. DU PONT DE NEMOURS & COMPANY, INC.,
WILMINGTON, DEL.

THE process of softening rubber has received much less study than its importance deserves. Since the method of softening rubber by mastication was devised by Hancock, the greatest advances have been in the introduction of machines of greater mechanical efficiency and greater capacity. Prior to 1920 the effect of such variables as temperature was little understood. Long and inefficient periods of milling at high temperatures were common. In case milling did not produce the required plasticity, recourse was had to the addition of oils, resins, and other soft materials sometimes in considerable amounts. Such conditions have not yet entirely disappeared.

Various methods have recently been proposed for plasticizing rubber in a more uniform manner and with less power consumption. Worthington and Hyde (24) softened rubber by heating it in a nonoxidizing atmosphere. Bradley and Ferrettie (1) concluded that the rubber should be water-soaked before it is heated and should be kept wet during the process. Tuley (21) patented the process of softening rubber by the addition of lead dioxide during the period of mastication, and Gerke (7) used a mixture of lead dioxide with an organic acid anhydride. Cruikshank (4) proposed the use of solvents containing alcohols of high molecular weight or sulfonated petroleum products as mastication assistants. According to Martin (10) the addition of nitrites to the latex before coagulation produces rubber of superior plasticity. Rubber softened by heating in an oxidizing atmosphere according to the method of Unger and Schidrowitz (22) has recently become a commercial product.

It had long been suspected that oxygen was a factor in softening by mastication. Thompson (20), Porritt (13), Fry and Porritt (6), Kohman (9), and Grenquist (8) expressed the opinion that rubber or some substance contained in the rubber was oxidized during the milling period. Fisher and Gray (5) showed that a small percentage of the double bonds became saturated when rubber was milled in contact with air.

It remained, however, for Cotton (3) and Busse (2) working independently to supply the final proof that oxygen is required for the softening of rubber by milling. They found

by milling rubber in an atmosphere of different gases or under reduced pressure that satisfactory softening resulted only in the presence of oxygen. Busse showed that peroxides were formed which in most cases persisted for several days. The types of rubber from which the peroxides disappeared most rapidly were found to be the most difficult to plasticize.

The method by which oxygen reduces the plasticity of rubber is not yet adequately explained. Ordinary exposure of rubber to air is ineffective. Exposure of rubber, while in a greatly swollen condition, or milling in the presence of air are essential for the efficient action of oxygen. Staudinger and Bondy (19) and Busse each believe that the long rubber molecule is broken by the action of oxygen. Busse believes that stretching during mastication activates both rubber and oxygen. Cotton showed that ozone was formed during milling but also found that ozonized air does not increase the rate of mastication. If a carbon-carbon bond is destroyed by the decomposition of peroxides, rubber will be expected to continue to soften as long as peroxides are present. Softening after the milling period is, however, contrary to general experience. No relation has yet been found between the amount of oxygen involved and the degree of softening produced. Since oxygen does not readily attack unstrained rubber, a simple relationship should exist if softening consists in a simple chemical action.

Unvulcanized rubber is either an association colloid or a true colloid of high molecular weight, but in either case the composition is not uniform in regard to the unit structure. The separation of rubber into sol and gel fractions is well known. Midgley, Henne, and Renoll (12) showed that rubber can be separated into a continuous series of products. Midgley and Henne (11) showed further that sol rubber can be separated into a series of fractions, each of which differs in solubility and tackiness, but each of which is still rubber. Although the gel fraction of rubber has received less study, it is known that milling in air, which involves oxidation, will change gel rubber to the sol form. It is possible then that rubber is a colloidal material consisting essentially of a single phase composed of two types of mutually soluble components, one of which is more highly attacked by oxygen than the other. The question of the micellar or molecular structure of rubber in very dilute solution is still an open question, but in the massive condition rubber exists in an associated form.

Since rubber is colloidal, it should be easily susceptible to changes in its physical properties. This is especially true if rubber is an association colloid in which the structure is due to the state of aggregation and in which a change in the attraction between the units could result in either increased or decreased mobility.

Various materials have been shown to affect the plasticity of rubber. Zimmerman and Cooper (25) showed that stearic acid has a considerable plasticizing action. They also showed

that substances such as *p*-aminophenol and benzidine have a considerable stiffening action. In the case of benzidine the maximum stiffening action is produced when 0.125 per cent is present. Increasing amounts up to 2 per cent cause a progressively decreasing stiffening. Similar results were obtained with *p*-aminophenol. Such results indicate that the action of these materials is physical rather than chemical.

The viscosity of rubber sols is also easily influenced by the presence of a large variety of substances. Spence and Kratz (16) observed that trichloroacetic acid would reduce the viscosity of rubber sols. Shimada (14) tested the effect of pyridine, piperidine, α -picoline, indole, skatole, and acridine on the viscosity of a benzene solution containing 0.45 gram of rubber in 100 cc. of cement and found that all except acridine reduced the viscosity. Propionic, butyric, valeric, chloroacetic, bromoacetic, *p*-bromobenzoic, and *o*-iodobenzoic acids also reduced the viscosity (15).

Many vulcanization accelerators act as peptizing agents on rubber either in the presence or absence of solvents, especially after the rubber has been disturbed by the combination of a small amount of sulfur (23). Piperidinium pentamethylene dithiocarbamate has little influence on the plasticity of unvulcanized rubber but will plasticize rubber in the early state of vulcanization. Benzoyl peroxide acts as a peptizing agent for rubber which is lightly vulcanized with benzoyl peroxide but is not a peptizing agent for rubber vulcanized with sulfur. Different materials are required to act as peptizing agents on rubber which has been disturbed by different chemical reactions.

Effect of Phenylhydrazine on Rubber Sols

Many substituted hydrazines act on rubber to cause a marked degree of softening or on rubber sols to cause a great decrease in viscosity. By a suitable choice of hydrazines a range of activity can be secured comparable with the range of activity to be found among the various accelerators of vulcanization.

The peptizing action of hydrazines on rubber sols depends on the previous oxidation of the rubber. Sol rubber sols in benzene are readily peptized by small amounts of phenylhydrazine. Dry gel rubber which has been exposed to air and afterward swollen in benzene in the absence of oxygen will not go into solution even in the presence of phenylhydrazine. If, however, the gel rubber after being swollen with benzene is shaken with air, it can be rapidly brought into solution under the influence of phenylhydrazine.

The action of phenylhydrazine on insoluble rubber is shown in the following experiment:

The insoluble layer which remained after four benzene extractions of pale crepe rubber while protected from oxygen was used for the test. The rubber content was found by evaporating a portion to be approximately 2.3 per cent. Ten cubic centimeters

of this layer were introduced into two glass tubes each 7 mm. in diameter and closed at one end. A small piece of Carborundum and 0.02 gram of phenylhydrazine were introduced into each tube which was then drawn out to a capillary preparatory to sealing. Each tube was then evacuated until approximately 0.5 gram of benzene had distilled out, the Carborundum in the bottom of the tube causing the bubbles to sweep the entire column of benzene. Tube *A* was sealed while being evacuated, but tube *B* was permitted to fill with air before being sealed. The air-filled tube began to show evidence of solution in 30 minutes, and after 5 hours the rubber was in the form of a smooth thin cement while the evacuated tube after one month was little

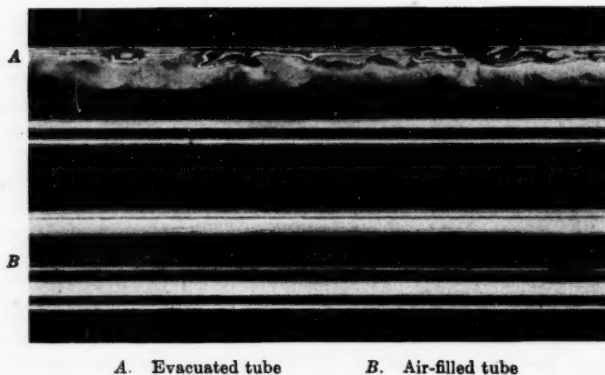


FIGURE 1. EFFECT OF PHENYLHYDRAZINE ON INSOLUBLE RUBBER

changed from the original lumpy condition. The condition of the two tubes after one month is shown in Figure 1. The photograph was made with the tubes in a horizontal position. The rough drainage of the cement in tube *A* is clearly shown whereas the cement in tube *B* is entirely smooth.

The reduction in viscosity of cements is usually accompanied by the development of a yellow color due to the oxidation of phenylhydrazine. This color appears to be caused by the action of free oxygen on phenylhydrazine since exactly the same color may be developed in benzene solutions containing no rubber. On the other hand, sol rubber may be peptized in evacuated tubes without the development of more than traces of color. One such cement initially had a relative viscosity of 8 seconds as measured by the time required for the vapor bubble to flow through the column of cement when the tube was inverted. After 8 hours the cement remained clear and the viscosity had reduced to 3 seconds, at which figure it remained after 24 hours. The admission of air caused the development of color and a final drop in viscosity to about 2 seconds.

Phenylhydrazine is effective in reducing the viscosity of dilute rubber sols:

A 2.7 per cent solution of sol rubber was prepared in dry benzene. After several weeks this was diluted to a concentration

TABLE I. REDUCTION IN VISCOSITY OF DILUTE RUBBER SOLS AT 56° C. UNDER THE INFLUENCE OF PHENYLHYDRAZINE

Minutes after Adding Phenyl- hydrazine	Viscosity in Seconds			Minutes after Adding Phenyl- hydrazine	Viscosity in Seconds		
	A	B	C		A	B	C
0	301.8	301.8	301.8	600	217.3	158.1	121.8
50	282.0	272.1	272.0	800	197.8	134.2	110.0
100	274.0	262.4	257.3	1000	183.6	124.8	109.1
250	265.9	252.3	241.0	2000	150.0	109.8	96.0
200	258.1	235.5	223.7	4200	113.7	94.5	87.2
400	237.8	198.0	159.0	8640	104.2	91.8	85.6

of 0.5 per cent and allowed to stand for 24 hours. Two hundred cubic centimeters of this cement were placed in each of three tubes which were surrounded by the vapor of boiling acetone. The tubes were closed with benzene-extracted corks which contained an opening for introducing nitrogen and an opening for the removal of samples. Tubes A, B, and C were treated with 0.02, 0.04, and 0.08 gram of phenylhydrazine, respectively, and were then flushed with nitrogen to insure uniformity in regard to contact with oxygen. Samples were withdrawn at intervals while nitrogen was being introduced into the tube. The sample was quickly cooled to 25° C. and the viscosity determined.

The viscosity was determined at 25° C. in a simple Ostwald viscometer which flowed a volume of 7.2 cc. under a mean head of 9.9 cm. through a capillary 4.5 cm. long and 0.608 mm. in diameter. The time of flow for benzene at 25° was 71.6 seconds.

The viscosity of each cement fell rapidly at first and after several days tended to approach an equilibrium. This equilibrium was more nearly reached and lowest in the cement containing the greatest concentration of phenylhydrazine. The apparent molecular weight determined according to the method of Staudinger (17) decreased from 115,000 to 4,300 for the greatest concentration of phenylhydrazine. The viscosity data are shown in Table I.

The viscosity of more concentrated cements is also reduced by the action of hydrazines. The magnitude of the effect increases somewhat with increasing amounts of reagent and a greater effect is produced by increasing the temperature.

Smoked sheet rubber was milled for 5 minutes on a laboratory mill at 70° C. and was then used to prepare a benzene cement containing 10 grams of rubber in 100 cc. of solvent. The cement was divided into portions which were treated with varying amounts of phenylhydrazine. The treated cements were then held at either 25° or 45° C. until an approximate equilibrium was reached. The relative viscosity was determined at 25° C. as the number of seconds required for a 3.18-mm. ($\frac{1}{8}$ -inch) steel ball to fall through a 15-cm. column of cement. The results are shown in Table II.

The effectiveness of phenylhydrazine as a peptizing agent for rubber cements depends considerably on the solvent. Gasoline cements are reduced less in viscosity than benzene cements. The addition of a small amount of an alcohol to the gasoline increases the reduction in viscosity. Lightly

TABLE II. EFFECT OF TEMPERATURE AND CONCENTRATION OF PHENYLHYDRAZINE ON VISCOSITY OF A RUBBER CEMENT

% Phenyl- hydrazine Based on Rubber Content	Viscosity in Seconds					
	Hours held at 25° C.			Hours held at 45° C.		
	0	23	48	240	12	23
0	72	72	71	70	68	69
0.2	72	13	11	6.5	6.7	4.5
0.4	72	8.6	4.0	2.0	2.1	1.3
0.8	72	8.8	2.5	1.1	1.1	0.8

milled smoked sheet rubber was used to prepare cements containing 10 grams of rubber in 100 cc. of different solvents. One per cent of phenylhydrazine based on the weight of rubber was added to the solvent before adding the rubber. The viscosity of the resulting cement, after standing at room temperature for 5 days, compared with a control containing no phenylhydrazine, is as follows:

Solvent	Viscosity in Seconds	
	No phenyl- hydrazine	1% phenyl- hydrazine on rubber content
Benzene	187	8
Gasoline	192	66
Gasoline containing 5% ethanol	121	19

Effect of Phenylhydrazine on Unswollen Rubber

The effect of phenylhydrazine on unswollen rubber is similar to the effect on rubber cements. Phenylhydrazine, whether added by diffusing in from the surface or by milling, produces more plastic rubber. In this case also the extent of softening depends on the condition of the rubber, concentration of reagent, and the temperature at which the softening is carried out. Hard types of rubber containing a large gel fraction are less readily plasticized by diffusing the reagent into the rubber. High temperatures promote more rapid action and generally result in increased softness. Softening begins as soon as the phenylhydrazine is milled into rubber, and in case the milling temperature is sufficiently high a considerable amount of softening will be accomplished during the milling period. Under any given set of conditions the degree of softening can be closely duplicated.

The effect upon the final plasticity and time required to reach equilibrium caused by milling phenylhydrazine into rubber is shown by the following experiment:

Fifteen hundred grams of pale crepe rubber were milled for 5 minutes on an 18-inch mill heated with water at 70° C. One per cent of phenylhydrazine was then added and the milling continued for 4 minutes. Portions of the rubber were placed in ovens at 25° and 70° C. and the plasticity was measured at frequent intervals. A similar test was run in which only 0.5 per cent of phenylhydrazine was used. These were compared with a control stock which was milled for 9 minutes but which contained no phenylhydrazine. The relative plasticities were ob-

tained as the thickness of a 2-cc. pellet after being in a parallel plate plastometer at 70° C. for 5 minutes. The data obtained are shown in Figure 2.

The data indicate that some softening was produced by the phenylhydrazine during the milling period. The action then continued at a relatively rapid rate until most of the softening action was completed, after which the rate diminished

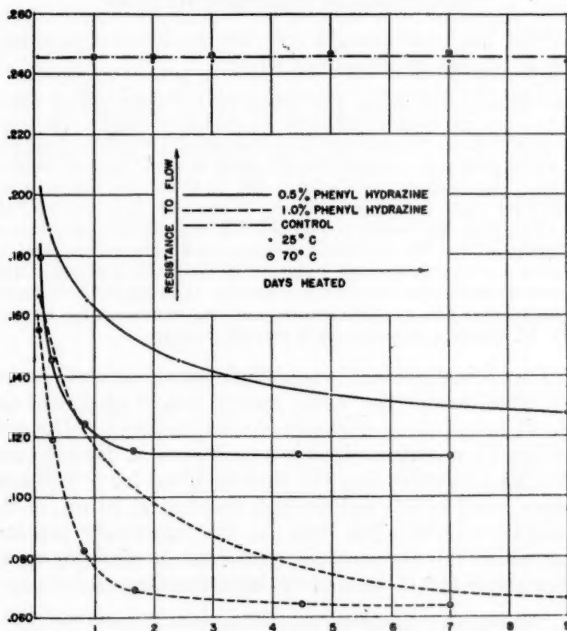


FIGURE 2. EFFECT OF PHENYLHYDRAZINE ON UNSWOLLEN RUBBER

and finally became almost zero. The higher temperature and greater amount of peptizing agent were the most effective.

The use of hydrazines to eliminate a portion of the milling period or to produce excessively soft rubber depends to a considerable extent upon the elimination of the gel fraction of the rubber before or during treatment. Rubber latex may be treated and a measure of softening obtained, but the condition of the rubber does not favor the best results. Many samples of pale crepe do not respond well to hydrazines which have been diffused in from the surface. A short period of milling either during or before the addition of the peptizing agent will be sufficient to reduce good-quality rubber to a relatively uniformly reactive condition. If very small amounts of hydrazines are used, they may be sufficiently destroyed during the milling period that little further softening will take place on storage. The use of larger amounts should

develop properties during storage similar to those shown in Figure 2.

Certain of the common compounding ingredients interfere with the normal action of hydrazines. This is especially true of carbon black, sulfur, and certain clays. For this reason peptizing agents should be permitted to soften the rubber before it is compounded.

Properties of Peptized Rubber

Rubber has been brought into the condition of a viscous liquid by means of phenylhydrazine:

Two hundred grams of pale crepe rubber were milled for 15 minutes on an 8-inch (20.3-cm.) laboratory mill. This was placed in 1500 cc. of benzene which contained 15 grams of phenylhydrazine and was stirred slowly until a thin smooth cement resulted. The cement was held at 40° to 45° C. for a month and was stirred daily for a few minutes in contact with air. At the end of this time the solution was poured into alcohol, and the resulting coagulum was washed five times in 2 liters of hot acetone in which it was soft enough to break up into small pieces. One per cent of phenyl- α -naphthylamine was then added to prevent oxidation, and the remaining acetone was removed by heating to 60° C. under a pressure of 2 cm. of mercury.

The resulting product was a dark amber-colored rubber which would readily flow under its own weight when cold and at 80° C. was of the consistency of thick molasses. The relative viscosity was determined in a tube 3 cm. in diameter and 30 cm. long by recording the time required for a 3.18-mm. (1/8-inch) steel ball to fall through the central 10 cm. of the column of rubber. The data on this extremely peptized rubber show the temperature coefficient of viscosity to be greater below 55° C. than above that temperature:

Temp., ° C.	Viscosity, Sec.	Temp., ° C.	Viscosity, Sec.
36.0	2257	56.1	238
45.0	1110	70.0	125
47.5	825	80.0	88

One hundred grams of the viscous rubber were compounded with 5 parts zinc oxide, 3 parts stearic acid, 5 parts sulfur, and 0.3 part tetramethylthiuram disulfide by working the rubber and ingredients on a glass plate with a spatula. A portion of this rubber was easily forced into a glass capillary at 60° C. where it was vulcanized to form a relatively strong thread. Dumb-bell strips cut from a slab vulcanized for 10 minutes at 130° C. gave a maximum tensile strength of 115 kg. per sq. cm. and a maximum elongation of 670 per cent. Excessively softened rubber appears to require somewhat more sulfur than normal rubber and has a tendency to break at a lower elongation.

The softness obtained with phenylhydrazine persists no more after vulcanization than the softness obtained by milling. Rubber softened by means of phenylhydrazine is equal in modulus and tensile strength to rubber softened the same amount by milling. However, rubber which has been sof-

tened an equal amount by a combination of milling and addition of softeners such as mineral oil remains much lower in modulus after vulcanization. The phenylhydrazine remaining in the rubber if relatively large amounts have been used may, however, either retard or accelerate the vulcanization, depending upon the particular accelerator employed so that an adjustment is required in the time of cure.

The effect of softening with phenylhydrazine on the properties of the vulcanized rubber is shown in the following experiment:

Rubber softened by milling for 30 minutes on a laboratory mill at 50° C. and rubber softened by incorporation of 0.5 per cent of phenylhydrazine followed by 24 hours at 50° C. each gave a plasticity of 0.084 as measured by the thickness of a 2-cc. pellet in the plasticity press for 5 minutes at 70° C. Each rubber was compounded by adding 5 parts of zinc oxide, 3 parts of sulfur, and 1 part of diphenylguanidine. The compounds were vulcanized for 45 minutes at 140° C. and were then aged in the oxygen bomb at 70° C. The results in each case were similar as shown by the data in Table III.

TABLE III. COMPARISON OF PROPERTIES OF MILLED AND PEPTIZED RUBBER AFTER VULCANIZATION

Time in Oxygen Bomb	Load at Elongation of: 600%	Elongation of: 700%	Tensile Strength	Elongation at Break
Days	Kg./sq. cm.			%
	Softened by Milling			
0	57	115	205	820
2	54	105	145	760
4	33	440
	Softened with Phenylhydrazine			
0	53	108	207	840
2	53	100	163	800
4	48	82	90	720

Effective Types of Hydrazines

A wide variety of substituted hydrazines will act as peptizing agents. Aliphatic hydrazines such as pentamethylene hydrazine are probably the most active, but monosubstituted aromatic hydrazines are almost equally effective. Phenylhydrazine is slightly more active than *m*- or *p*-tolylhydrazine and is considerably more active than *o*-tolylhydrazine or the naphthylhydrazines. *asym*-Diphenylhydrazine and *sym*-phenylethylhydrazine are equal to *o*-tolylhydrazine in activity. On the other hand, *sym*-diphenylhydrazine and tetraphenylhydrazine produce a stiffening action.

Many substituted hydrazine derivatives are effective softeners. Either the organic or inorganic salts are usually almost as effective as the free base. The addition products formed with phenols, carbon dioxide, carbon disulfide, and sulfur dioxide are moderately strong softeners. The complex salts formed by adding the hydrazine to a heavy metal salt are as effective as their hydrazine content. An example of this type is the solid resulting from the addition of 2 moles of phenylhydrazine with 1 mole of zinc chloride or sulfate. The

hydrazones have a varied activity which ranges from moderately strong in the case of such derivatives as α -ethyl- β -propylacrolein phenylhydrazone to very weak for products such as acetone phenylhydrazone.

The use of peptizing agents should permit rubber to be softened sufficiently that the ordinary softeners such as mineral oils, tars, and stearic acid can be avoided. This should permit the development of compounds which are superior for many purposes to those now in use. Swelling agents such as mineral oils probably serve to weaken the rubber. Some evidence exists that a large amount of soluble zinc salts, such as will be obtained in the presence of stearic acid, have a harmful effect on rubber in regard to aging and resistance to flex cracking. The elimination of softeners, however, will require a study to determine the appropriate changes in volume and type of fillers and acceleration.

Possible Methods of Action

Three methods by which phenylhydrazine could increase the mobility of rubber are possible:

1. The hydrazine may react chemically to assist in the destruction of a carbon-carbon bond in the rubber molecule.
2. The hydrazine may react chemically without the rupture of a carbon bond in such a manner that the attraction between molecules of rubber is decreased.
3. The hydrazine may act in a purely physical manner to decrease the intermolecular forces in the rubber.

The rupture of a carbon bond depends upon the action of oxygen assisted in some manner by the hydrazine. Phenylhydrazine does not act only as an oxygen carrier because sol rubber will peptize in the absence of free oxygen. The unstable portion of the rubber molecule as suggested by Staudinger (18) is between the two carbon atoms which carry two hydrogens each. However, the addition of oxygen at the double bond should serve to strengthen this weak position and make it more probable that the rupture would occur at the position of the double bond. The decomposition of a peroxide formed at the double bond into an aldehyde and a ketone group might be assisted by the hydrazine, owing to reaction either with the peroxide or the resulting decomposition products. The nitrogen content of extracted peptized rubber seems to be slightly greater than that of the original rubber. The rupture of the hydrocarbon chain could adequately explain the reduction in viscosity of a dilute rubber sol, but the effect of such a decrease in molecular size on the mobility of massive polymer is problematical.

Hydrazines may act to vary the forces between molecules of an associated group. Such a mechanism could assist in the final separation of rubber molecules into a more nearly true solution and account for the increased mobility of massive rubber. This action also must involve oxygen and may

involve chemical action of the hydrazine. If the forces of intermolecular association are centered largely in the double bonds, it can be understood that the addition of oxygen would reduce the attraction. Reduction of the peroxide by the hydrazine, followed by a further possible addition of hydrazine to the resulting oxide, might cause an additional weakening of the attraction. It is improbable that the hydrazines act simply as reducing agents since such reducing agents as hydrogen iodide or moderate catalytic hydrogenation have much less effect on the mobility of the rubber.

The action may be partly physical in nature. Such physical effects are found in the stiffening action of such substances as tetraphenylhydrazine or hydrazobenzene. Such an explanation of the softening action of phenylhydrazine is, however, weakened by the inability to remove the hydrazine and return the rubber to its original stiffness.

It is probable that the increase in mobility is brought about by chemical activity of the hydrazine. Such a process would not be reversible. Whether the hydrocarbon chain is broken or not, the presence of either the hydrazine or its reaction products serve materially to decrease the attraction between the rubber molecules.

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Hard Rubber

Its Carbon and Hydrogen Content

Harry L. Fisher and Y. Schubert

UNITED STATES RUBBER PRODUCTS, INC., PASSAIC, N. J.

IN THE course of a study of vulcanization it became necessary to compare the ratios of carbon, hydrogen, and sulfur in hard rubber. A search of the literature revealed no analyses for carbon and hydrogen, although many analyses for sulfur in hard rubber have been recorded. Combustion analyses were therefore made on several samples of hard rubber, and the data are recorded here.

The saturation of the double bonds in the rubber hydrocarbon with sulfur should give a compound, $(C_5H_8S)_x$, which contains 32.02 per cent of combined sulfur, and some of the recorded results agree with this figure. Since it is also possible to obtain products having greater amounts of combined sulfur than that called for by the theory of addition alone, some of the sulfur must consist of sulfur of substitution (?). It is theoretically possible that substitution and addition of sulfur can go on simultaneously; as the result of these two reactions, it may happen that the total sulfur in combination will equal the theoretical amount required by addition alone. In such a case there would be some free double bonds, but attempts to determine free double bonds in several samples by the Kemp-Wijs method (5) were unsuccessful.

If there is any substitution, there must be less hydrogen. Therefore, it should be possible to tell by the carbon and hydrogen content whether there has been any substitution, since the hydrogen would be low. There are difficulties, however, in the interpretation of the data, because there are variations in the analyses on account of the loss of hydrogen sulfide after the sample has been vulcanized (2, 10), the continued loss of sulfur by acetone extraction (7), and the presence of protein and other nonrubber constituents.

If there is substitution, hydrogen sulfide must be formed as a by-product. It is well known that hydrogen sulfide is practically always noted when hard rubber is removed from a mold (10). In this connection a recent note from the National Bureau of Standards (1) gives some interesting data. A slab of hard rubber mix, containing 68 parts of fine Para rubber and 32 parts of sulfur, 1 mm. thick, was vulcanized between alumi-

num plates in a press at 148°C. , and the loss in weight determined periodically. At the end of 25 hours the loss was 0.045 per cent, and in 47 hours, 0.295 per cent. This loss was no doubt due chiefly, if not entirely, to hydrogen sulfide. Also, a sample of the same stock was extruded in a layer 1 mm. thick around an aluminum wire and heated in an inert atmosphere at the same temperature. The hydrogen sulfide given off was determined by absorption in alkali and was found to amount to 0.47 per cent in 4 hours, 1.85 per cent in 26 hours, and 3.06 per cent in 50 hours. No analyses for combined sulfur were recorded. It is hoped that the source of all this hydrogen sulfide will be cleared up by further work at the bureau, and also that it will be shown whether similar results are obtained with purified rubber hydrocarbon.



ARTICLES OF HARD RUBBER

Left to right: T and elbow; float ball, flange, and brush handle; battery jar for miner's lamp and stopcock.

Weber (8), whose figures are probably the earliest recorded, obtained on three separately prepared acetone-extracted samples of hard rubber, 33.08, 33.11, and 32.64 per cent of combined sulfur; Spence and Young (6), using acetone-extracted rubber as their starting material, found 31.91 and 31.97; Hinrichsen and Kindscher (4), working with rubber in solution at 170°C. and using approximately ten and eight times the theoretically required amount of sulfur, obtained 31.92 and 31.66, respectively; and Whitby and Jane (9), also using solutions and a large excess of sulfur, found not over 32.4 per cent of sulfur. Stevens and Stevens (7) showed that with the use of large proportions of sulfur and an ultra-accelerator, at a comparatively low temperature (100°C.), the coefficient of vulcanization could be raised to considerably over 47.1:¹ "The amount of sulfur combined with the rubber, given sufficient heating and presence of accelerator, is mainly dependent on the excess of sulfur present." At 70°C. these authors found that the coefficient did not rise above 46.4, even in 336 hours.

Experimental Procedure

The four samples used for analysis were all vulcanized at 141° C. The amount of sulfur was the theoretical amount in one case, *A*, slightly in excess of the theoretical amount in another, *B*, and approximately 50 per cent in excess in the other two, *C* and *D*. Stearic acid was added in case *D*. Otherwise, no accelerator and no zinc oxide were used. The recipes were as follows:

	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
Purified rubber hydrocarbon	100	100	100	100
Pale crepe	...	100	100	100
Sulfur	47	50	75	75
Stearic acid	10

Sample *A* was prepared by Cummings (2) from purified rubber hydrocarbon (99.5 per cent) at the National Bureau of Standards. It was vulcanized as a sheet, 0.33 mm. thick, between thin aluminum plates in a press for 40 hours at 141° C. It was almost black and very tough.

Samples *B*, *C*, and *D* were prepared in the usual laboratory manner, and each was vulcanized as a sheet, approximately 2.5 mm. thick, between tin in a press for 9 hours at 141° C.

TABLE I. PERCENTAGE ANALYSES OF HARD RUBBER SAMPLES

Sample:	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
Carbon	...	{ 57.85 } 57.90 { 57.94 }	{ 52.13 } 52.17 { 52.21 }	{ 53.20 } 53.34 { 53.47 }
Hydrogen	...	{ 7.56 } 7.69 { 7.81 }	{ 7.01 } 7.10 { 7.18 }	{ 7.10 } 7.25 { 7.39 }
Total sulfur	{ 32.15 } { 32.30 }	32.23 { 33.00 } { 33.14 }	33.07 { 39.13 } { 39.49 }	39.31 { 39.00 } { 39.28 }
Total		98.66	98.58	99.73
Acetone extract	1.39	5.61	12.61	16.71
Free sulfur (66-hr. acetone extr.)	{ 0.88 } { 1.05 }	0.97 { 3.95 } { 3.95 }	3.95 { 10.55 } { 10.85 }	10.70 { 9.33 } { 9.46 }
Sulfur (crystalline) which had sublimed and was adhering to surface of sample	0.00	0.05	0.17	0.12
Total sulfur added (calcd.)	31.97	33.33	42.86	40.54

The samples for analysis were finely divided with a rasp file, any metal particles were removed with a magnet, and the material was then extracted with acetone. The extractions for the first set of analyses were run for the customary length of time for extracting hard rubber, about 66 hours. Later, samples *C* and *D* were extracted continuously for 1680 hours more, making 1746 hours in all, and both elemental sulfur and sulfate ion could be detected even in the final extract. These extractions are approximately half again as long as those described by Stevens and Stevens (7), and the results in general corroborate their work.

The combustions were carried out in oxygen using cerium dioxide on pumice as the catalyst, followed in the tube with cupric oxide wire and a mixture of lead dioxide and minium, in accordance with the directions outlined by the senior author (3). No difficulties were encountered.

The procedure for determining combined sulfur was as follows: 0.3 gram of the sample, 15 grams of sodium peroxide, and 0.9 gram of pulverized sucrose were mixed well in a Parr bomb, and the mixture was ignited by heating the closed bomb with a fine blast lamp flame. The bomb was cooled in running water, the

fused mass taken up with distilled water, the solution acidified and treated with barium chloride as usual.

Nitrogen was determined by the Kjeldahl method.

Analyses of the original samples of hard rubber are given in Table I.

The analyses for total sulfur agree well with the sulfur added in samples *A* and *B*, but in *C* and *D* the difference is 3.38 and 1.28, respectively, taking into account the amount of sublimed sulfur found on the surface of the samples. No attempt was made to catch and determine the amount of hydrogen sulfide given off during vulcanization, and therefore the question as to whether the losses are attributable to hydrogen sulfide cannot be answered.

Analyses of the acetone-extracted samples are given in Table II. The calculations are based on the weight of the dry extracted samples.

Discussion of Results

In Table II the combined sulfur is less than 32.02 per cent in samples *A* and *B*, and in *C* after the long extraction. The sulfur originally added in both *A* and *B* was approximately the theoretical amount to cause complete saturation of the double bonds, and sample *A* was vulcanized for the long period of 40 hours at 141° C.; yet the reaction is incomplete.

Also in Table II the combined sulfur in samples *C* and *D* after the 66-hour extraction is greater than 32.02 per cent; after the 1746-hour extraction the combined sulfur has dropped 1.41 and 1.07 per cent, respectively; and this drop brings the combined sulfur in *C* under 32.02 per cent.

There are certain nonrubber constituents in the rubber, and sulfur reacts with some of these to give off hydrogen sulfide. How much sulfur is thus combined and how much hydrogen sulfide may come from this source are questions which have not been answered.

Except in sample *A*, the rubber used was ordinary pale crepe which contains approximately 5 per cent nonrubber constituents. Acetone extraction probably removes a little over half of this amount, but it is probable that the rest, consisting chiefly of protein, remains. Assuming that all the protein remains in the hard rubber, it has been calculated that, on the basis of the average composition of protein, the protein carbon would be equal to about 0.8 per cent, hydrogen 0.12, nitrogen 0.25, and oxygen 0.30. The amount of hydrogen is within the combustion error, but the amount of carbon is greater in proportion and may introduce a serious error. Since the actual amount of nitrogen found is less than the calculated amount, it may be that a portion of the protein has been changed and has been removed by the acetone extraction.

¹ The coefficient of vulcanization is the number of parts of combined sulfur referred to 100 parts of rubber hydrocarbon, and, therefore, 47.1 corresponds to 32.02 per cent of combined sulfur in the saturated rubber sulfide.

TABLE II. PERCENTAGE ANALYSES OF ACETONE-EXTRACTED SAMPLES

Sample:	A ^a	B ^a	C ^a	C ^b	D ^a	D ^b
Carbon	{ 60.32 60.21 8.11 }	{ 60.80 60.75 8.05 }	{ 60.78 58.00 2.78 }	{ 59.16 59.37 8.10 }	{ 57.67 57.61 7.70 }	{ 58.73 58.66 8.01 }
Hydrogen	{ 8.96 8.90 0.06 }	{ 8.10 7.89 0.21 }	{ 8.14 7.80 0.34 }	{ 8.10 8.29 30.97 }	{ 7.86 7.80 33.68 }	{ 8.06 7.78 32.69 }
Sulfur	{ 31.40 31.54 }	{ 29.47 29.39 }	{ 29.43 28.54 }	{ 32.39 30.99 }	{ 30.98 28.43 }	{ 32.62 28.38 }
Total	99.83	98.35	98.17	98.17	98.43	99.38
Nitrogen	...	{ 0.17 0.18 }	{ 0.16 0.20 }	{ 0.18 0.41 }	{ 0.13 0.17 }	...
Ash	0.10	{ 0.50 0.57 }	{ 0.40 0.42 }	0.41	{ 0.36 0.43 }	0.33
Grand total	99.93	99.07	98.76	98.76	99.24(7)	99.71
C, H, S calcd. to total of 100:						
Carbon	60.37	61.80	59.06	60.24	58.16	59.07
Hydrogen	8.10	8.28	7.95	8.31	7.85	8.11
Sulfur	31.53	29.92	32.99	31.45	33.99	32.82
Total	100.00	100.00	100.00	100.00	100.00	100.00
Ratio C:H:S	5.00:7.99:0.98	5.00:7.87:0.90	5.00:8.02:1.05	5.00:8.22:0.98	5.00:8.03:1.09	5.00:8.18:1.04

Theory for:
 $(\text{C}_6\text{H}_5\text{S})_2$ $(\text{C}_6\text{H}_7\text{S})_2$ $(\text{C}_6\text{H}_8\text{S})_2$

Carbon
Hydrogen
Sulfur
Total
Nitrogen
Ash
Grand total

C, H, S, calcd. to total of 100:			
Carbon	59.92	60.54	61.15
Hydrogen	8.06	7.12	6.17
Sulfur	32.02	32.34	32.68
Total	100.00	100.00	100.00
Ratio C:H:S	5.00:8.00:1.00	5.00:7.00:1.00	5.00:6.00:1.00

^a Sample extracted 66 hours. ^b Sample extracted 1746 hours.

In this connection, there seems to be no way of knowing how much sulfur is combined with the protein and how much of the protein (free and sulfurized) remains in the extracted sample.

The data given in the tables appear to show that in the formation of hard rubber, when the amount of sulfur mixed with the rubber is approximately the theoretical (32.02 per cent), it adds to the rubber hydrocarbon until saturation is complete; very little, if any, substitution takes place. When the amount of sulfur mixed with the rubber is greater than the theoretical, the combined sulfur is greater than 32.02 per cent, indicating that some of it has substituted for hydrogen. Hydrogen sulfide is formed all during the reaction, and this means substitution. The hydrogen sulfide may, of course, come from the action of sulfur on the nonrubber constituents. The use of purified rubber hydrocarbon should answer this question.

The last portion of sulfur adds very slowly. The reaction in sample A, even after 40 hours, is still incomplete, although approximately 1 per cent of sulfur remains uncombined.

Further work is in progress on the analysis of other samples of hard rubber, and it is hoped that some of the questions raised here may be answered in a future publication.

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